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TORREFACTION STUDIES OF VARIOUS OIL PALM BIOMASS

by

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A Thesis

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DECLARATION OF THESIS

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DEDICATION

With gratitude and love,

This success is dedicated to my beloved family and friends.

ABSTRACT

Oil palm biomass are the main agricultural wastes in Malaysia. However, biomass have relatively high moisture content, low energy density and durability against biodegradation. To overcome these problems, a pre-treatment method called as torrefaction process was applied in this work. Torrefaction process of empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) of size range 250-500 μm were performed under inert atmosphere at mild torrefaction (200, 220 and 240 °C) and severe torrefaction (260, 280 and 300 °C) in the TGA and tube furnace. The objectives of this research work were to investigate the changes in the properties of torrefied biomass included CHNS content, calorific value, weight loss distribution, mass and energy yield, mass loss and internal structure. Torrefaction behavior and its kinetic have been studied and a model was proposed to predict the produced amount of torrefied biomass. This research work found that as the torrefaction temperature increase, the carbon content and calorific value increased whereas the O/C ratio, hydrogen and oxygen contents of EFB, PMF and PKS decreased. Both EFB and PMF gave the highest mass loss than PKS under severe torrefaction. The research work proposed that the mass loss was an excellent indicator for the torrefaction severity. Due to high mass loss of both EFB and PMF, they also gave lower mass yield than PKS. The energy yield of PKS could be maintained within the range of 86-92% from mild to severe torrefaction, until 280 °C. However, the energy yields of both EFB and PMF could be only maintained within the range of 70-78% at mild torrefaction, until 240 °C. Besides, torrefaction at 300 °C was not recommended, since it caused very high mass loss which was more than 45% and produced very low energy yield which was less than 70%. Moreover, the SEM images verified that the impact of torrefaction on the internal structure of both EFB and PMF were more significant than PKS under severe torrefaction. In general, the research work concluded that these differences properties of torrefied oil palm biomass were mainly dependant on four parameters i.e. torrefaction temperature, biomass type, composition and decomposition temperature of hemicellulose, cellulose and lignin.

Furthermore, a model was developed for torrefaction process of oil palm biomass which based on a two-stage decomposition reaction. The first is the fast stage which represented by hemicellulose decomposition while the second is the slow stage which represented by charring of the hemicellulose fraction. The developed model successfully represented torrefaction process for EFB, PMF and PKS at particle size of 250-500 μm with calculated absolute average deviation (AAD) below than 5%. Therefore, the developed model could be applied to predict the amount of torrefied biomass at the selected torrefaction temperatures.

ABSTRAK

Biomas kelapa sawit adalah sisa pertanian yang utama di Malaysia. Walau bagaimanapun, biomas ini mempunyai kandungan kelembapan yang tinggi, intensiti tenaga dan ketahanan terhadap biodegradasi yang rendah. Bagi mengatasi masalah ini, kaedah pra-rawatan iaitu proses torrefaksi telah digunakan. Proses torrefaksi tandan kosong buah kelapa sawit (EFB), mesocarp fiber kelapa sawit (PMF) dan kulit kernel kelapa sawit (PKS) pada julat saiz 250-500 μm telah dilaksanakan dalam atmosfera lengai pada proses torrefaksi rendah (200, 220 dan 240 °C) dan proses torrefaksi tinggi (260, 280 dan 300 °C) di dalam TGA dan tiub relau. Objektif penyelidikan ini adalah menyiasat perubahan cirri-ciri pada biomas yang telah menjalani proses torrefaksi termasuk kandungan CHNS, nilai kalori, taburan kehilangan berat, hasil jisim dan tenaga, kehilangan jisim dan struktur dalaman. Penyelidikan terhadap tingkah laku torrefaksi dan kinetik turut dijalankan serta sebuah model telah dicadangkan untuk meramal jumlah biomas selepas proses torrefaksi. Penyelidikan ini telah melaporkan bahawa apabila suhu torrefaksi meningkat, kandungan karbon dan nilai kalori bertambah manakala nisbah O/C, kandungan hidrogen and oksigen untuk EFB, PMF dan PKS menurun selepas proses torrefaksi. Kedua-dua EFB dan PMF mempunyai kehilangan jisim yang paling tinggi daripada PKS pada proses torrefaksi tinggi. Penyelidikan ini telah mencadangkan bahawa kehilangan jisim adalah penunjuk yang baik untuk tahap intensiti proses torrefaksi. Disebabkan kehilangan jisim yang tinggi oleh kedua-dua EFB dan PMF, mereka juga mempunyai hasil jisim yang rendah daripada PKS. Hasil tenaga PKS boleh dikekalkan pada julat 86-92% daripada proses torrefaksi rendah ke tinggi sehingga pada suhu 280 °C. Walau bagaimanapun, hasil tenaga kedua-dua EFB dan PMF hanya boleh dikekalkan pada julat 70-78% sehingga proses torrefaksi rendah pada suhu 240 °C. Selain itu, proses torrefaksi pada suhu 300 °C tidak disyorkan kerana menyebabkan kehilangan jisim yang tinggi iaitu lebih daripada 45% dan menghasilkan hasil tenaga yang rendah iaitu kurang daripada 70%. Tambahan pula, imej-imej SEM membuktikan bahawa kesan torrefaksi pada struktur dalaman kedua-

dua EFB dan PMF adalah lebih ketara daripada PKS pada proses torrefaksi tinggi. Secara umumnya, semua perbezaan ciri-ciri biomas kelapa sawit selepas proses torrefaksi adalah bergantung kepada empat parameter iaitu suhu torrefaksi, jenis biomas, komposisi dan suhu penguraian hemiselulosa, selulosa dan lignin. Penyelidikan ini juga membangunkan satu model untuk proses torrefaksi biomas kelapa sawit berdasarkan kepada dua peringkat tindak balas penguraian. Peringkat pertama ialah proses yang cepat iaitu mewakili penguraian hemiselulosa manakala peringkat kedua ialah proses yang perlahan iaitu mewakili penguraian lagi pecahan hemiselluosa. Model yang dibangunkan telah berjaya mewakili proses torrefaksi untuk EFB, PMF dan PKS pada julat saiz 250-500 μm dengan nilai AAD kurang daripada 5%. Oleh itu, model ini boleh digunakan untuk meramal jumlah biomas yang terhasil untuk setiap suhu torrefaksi yang dipilih.

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LIST OF ABBREVIATIONS

EFB	Empty fruit bunches
PMF	Palm mesocarp fiber
PKS	Palm kernel shell
TGA	Thermogravimetric analyzer
CHNS Analyzer	Carbon, hydrogen, nitrogen, sulphur analyzer
SEM	Scanning electron microscope
ASTM Standard	American society of testing materials
GCV	Gross calorific value
HHV	High heating value
wt. %	Percentage of weight
O/C ratio	Oxygen per carbon ratio
ML	Mass loss
Y_{mass}	Mass yield
Y_{energy}	Energy yield
AAD	Absolute average deviation

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

In the transition process to sustainable energy supply, an alternative energy from renewable resources has attracted wide interest across the world. The utilization of renewable energy resources becomes more urgent due to energy crisis and environmental problems such as global warming and pollutant emission. It is also important to promote renewable energy, in order to substitute the depleting resources of fossil fuel such as crude oil and natural gas (Yusoff, 2006; Sumathi et. al., 2008). Biomass utilization also is one of the viable options that can be developed to support the renewable energies sector. Energy generation from biomass has great potentials to substitute fossil fuel as it is abundant, clean and carbon dioxide neutral (Sulaiman et. al., 2011; Mohammed et. al., 2011; Shuit et. al., 2009; Demirbas, 2009). For instance, wood, energy crops, as well as agricultural residues are the examples of biomass resources that are abundantly available. Among these biomass, the residues from agricultural sectors are seem to be the most feasible feedstock to be utilized as the renewable energy resources.

Malaysia is blessed with a plentiful supply of renewable energies including biomass energy, solar, wind and hydropower (Shuit et. al., 2009; Yusoff, 2006). At present, the utilization of biomass from palm oil industry as an alternative fuel is widely been investigated and developed in Malaysia. The type of biomass produced from palm oil industry includes frond, trunk, empty fruit bunches (EFB), fiber, shell, and kernel (Sulaiman et. al., 2011; Mohammed et. al., 2011; Shuit et. al., 2009). The government has taken continuous effort to implement renewable energy supply.

through various programmes such as Small Renewable Energy Programme (SREP), Biomass-Based Power Generation and Cogeneration (Biogen) and Green Building Index (GBI) (Mohammed et al., 2011; Shuit et. al., 2009). In addition, in the eighth Malaysian plan, renewable energy had been announced as the fifth fuel under energy supply mix in the new Five Fuel Strategy. Through these supports and promotion programmes, it can increase an awareness of the importance of renewable energy sector to the nation.

According to Zhang et. al. (2010), biomass energy can be defined as the solar energy stored in the form of chemical energy, which can be released when the chemical bonds of oxygen, carbon, and hydrogen molecules are broken by various thermo-chemical and biological processes. The energy conversion technologies that applied for biomass utilization as fuels can be classified into three main processes such as thermochemical, biochemical or biological and mechanical conversion (Chew and Doshi, 2011; Demirbas, 2009). The form of biomass fuels can be either solid, liquid or gas depending on the conditions and parameters of the conversion technologies. In particular, biomass can be converted into gas products by gasification and transformed into liquid fuels such as biooil, biodiesel and bioethanol, via pyrolysis, liquefaction, trans-esterification as well as fermentation and saccharifaction (Mohammed et. al., 2011; Demirbas, 2009).

However, the raw biomass often reveals undesirable properties that hinder their utilization as feedstock for fuel production. In most cases, the raw biomass have high moisture content and low heating value. The high moisture content can cause storage complications such as biodegradation and self heating that attributes difficulty in handling (Chen and Kuo, 2010a; Arias et. al., 2008; Bridgeman et. al., 2008). They also have high O/C ratio and low energy density (Chen et. al., 2011a; Deng et. al., 2009; Bridgeman et. al., 2008). In addition, very high load amounts of the raw biomass are required to generate an equivalent amount of energy as fossil fuel such as coal (Deng et. al., 2009). Another important aspect is the grindability of biomass. Due to the fibrous and tenacious nature of the raw biomass, it is very difficult to grind biomass into small homogenous particle size (Arias et. al., 2008).

It is crucial to reduce the size especially when biomass is to be used in pulverized system such as co-firing with coal (Deng et. al., 2009). Therefore, without any pretreatment process, all of these aspects contribute limitations during the biomass utilization.

In order to improve the quality of biomass as feedstock, various pre-treatment methods of biomass have been proposed by researchers. In general, the pre-treatment methods will modify the physiochemical properties of the raw biomass. Chen et. al., (2011a) has reported that the physical pretreatment methods including dewatering and drying, pulverization, torrefaction and pelletization. Moreover, the biochemical pretreatment method such as dilute acid pretreatment also has been used for bioethanol production. Among these pre-treatment methods, torrefaction process is the most recommended method to improve the physiochemical properties of raw biomass as the feedstock for fuel production. In particular, torrefaction is a heat treatment process for biomass that performs at low temperature ranges between 200 to 300°C. It is carried out under atmospheric condition in the absence of oxygen. (Chen and Kuo, 2010; Deng et. al., 2009; Bridgeman et. al., 2008).

According to Prins et. al. (2006a), the products of torrefaction process consist of dark colour solid; condensable liquid including acetic acid, acetaldehyde, formic acid, methanol and acetone; and non-condensable gases which are mainly CO_2, CO and small amounts of CH_4 and H_2. Torrefaction process modifies the physiochemical properties of biomass such as decreases the mechanical property that improves the grindability and homogeneity, produces hydrophobic solid product with higher energy density and higher calorific value, and can enhance ignitibility and reactivity during gasification (Chew and Doshi, 2011; Uemura et. al., 2011; Chen and Kuo, 2010a; Arias et. al., 2008). Bridgeman et. al. (2008) has also reported that the torrefied biomass can be compacted into high grade pellets with better quality and characteristics compared to the standard wood pellets. This process is a combination of the techniques of drying, torrefaction and pelletization (TOP).

1.2 Problem Statement

It is known that pre-treatment methods have been applied to improve properties of raw biomass in biomass fuel production. Torrefaction process is one of the proposed pre-treatment that successfully improved the physiochemical properties of the untreated biomass. Despite all the reported studies, fundamental studies on torrefaction of oil palm biomass namely empty fruit bunches, mesocarp fiber and kernel shell are rather limited. A study that focuses on the influence of torrefaction temperature on the properties of torrefied oil palm biomass have not been studied. For example, understanding on the decomposition of oil palm biomass during torrefaction process and the changes in elemental composition and calorific value, mass and energy yields, mass loss and surface structure were not highlighted. Moreover, less attention has been paid on the kinetic study and modelling for torrefaction of oil palm biomass. The development of a kinetic model of torrefaction process is also important to predict the production yield of torrefied biomass. Therefore, a study that focuses in these shortcomings will enhance the understanding on the oil palm biomass torrefaction principles for further industrial applications.

1.3 Objectives

Torrefaction process has been widely applied as a pretreament method prior to further processes such as transportation, grinding or thermochemical conversion. In the present work, torrefaction process of three kind of oil palm biomass namely empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) are studied. The specific objectives of the present work are as follows:

i. To determine the properties of the raw oil palm biomass such as calorific value, proximate, ultimate and lignocellulosic analyses as well as SEM observation.
ii. To conduct torrefaction process in the tube furnace and TGA.
iii. To investigate the relationship between the properties of the torrefied biomass with the effects of torrefaction temperature, composition and decomposition temperatures of hemicellulose, cellulose and lignin in the EFB, PMF and PKS.

iv. To study the properties of torrefied biomass including the elemental composition, calorific value, mass loss, surface structure, weight loss distributions, mass and energy yields.
v. To study the weight loss kinetic of torrefaction process and develop a kinetics model based on two stages decomposition reaction as well as to predict the produced amount of torrefied biomass.

1.4 Scope of Work

Torrefaction process is performed under atmospheric condition under an inert condition with the flow rate of nitrogen gas of 100 ml min^{-1} and the heating rate of 10 °C min^{-1}. There are two different torrefaction conditions which are mild torrefaction process (200, 220 and 240 °C) and severe torrefaction process (260, 280 and 300 °C). The main scopes of this research work are:

i. Characterizations of raw oil palm biomass such as calorific value, proximate, ultimate analysis and lignocellulosic analyses as well as SEM observation.
ii. Torrefaction process is conducted in tube furnace to produce significant amount of torrefied biomass while in the TGA, the aim is to study the weight loss of oil palm biomass during torrefaction process.
iii. Characterizations of the torrefied biomass by conducting the ultimate analysis, calorific value, SEM observation and also analyzing the mass loss, weight loss distributions, mass and energy yields.
iv. Investigation on the effects of the torrefaction temperature, composition and decomposition temperatures of the hemicellulose, cellulose and lignin to the properties of the torrefied biomass.
v. Study on the weight loss kinetic of torrefaction process and develop a kinetics model based on two-stage decomposition reaction.

1.5 Organization of the Thesis

This dissertation consists of five chapters.

In chapter 1, the research backgrounds on the potential of biomass as sources of renewable energy, drawback properties of raw biomass and torrefaction process as the pretreatment method for biomass are described. The problems with the limited fundamental studies on torrefaction of oil palm biomass are highlighted. Furthermore, the objectives and scope of study to the research are also been reported in this chapter.

In chapter 2, the theoretical aspects and detail backgrounds about the present work are presented. It begins with an energy scenario in Malaysia, an overview of oil palm biomass and utilization of biomass energy. It follows with discussion on the issues faced with biomass utilization and the available pretreatment methods for biomass. The chapter also described an overview and perspective about torrefaction process and the stages involved in torrefaction process. The improved properties of torrefied biomass, characterization of torrefied biomass by several analysis and reviews on the mathematical models for torrefaction kinetic are also presented.

In chapter 3, the experimental works and description on the procedures for every analysis conducted are highlighted. The chapter begins with sample preparation of biomass, experimental procedure for torrefaction process by using TGA and tube furnace and procedures for every analysis to characterize raw and torrefied biomass. The procedures include proximate and ultimate analysis, calorific value determination and SEM observation. The calculation for the kinetic parameters such as reaction order, rate constant, activation energy and pre-exponential factor are also presented.

In chapter 4, the findings and outcomes of torrefaction process of oil palm biomass and its characterizations are highlighted. The characterizations of feedstock such as the composition of hemicellulose, cellulose and lignin are described in lignocellulosic analysis while the CHNS content, volatile matter, moisture content,

fixed carbon and ash content are described in the ultimate and proximate analysis; respectively. The details temperature profile of torrefaction process is also presented. The properties of torrefied biomass include the CHNS content, calorific value, weight loss, mass and energy yields, distributions weight loss, mass loss and internal structure are discussed. Moreover, the obtained value of kinetic parameters, a model that represents torrefaction process and comparison of the experimental and model data by the absolute average deviation (AAD) are also presented. Last but not least, the advantages or added values of torrefied oil palm biomass from these findings and its benefits for an industrial scale are also discussed.

In chapter 5, conclusions of the thesis are made based on the overall results and analysis that have been particularly discussed in this thesis. The possible future works which can be further conducted also have been suggested in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Chapter Overview

In the last two decades, numerous research activities on the renewable energy supply, biomass energy and pretreatment method for biomass such as torrefaction process have been conducted. In the present work, the energy scenario in Malaysia and an overview of oil palm industry and its biomass are presented in Section 2.2 and Section 2.3, respectively. The understanding about biomass energy, issues faced with the biomass utilization and the available pretreatment methods for biomass are discussed in Section 2.4. The principle of torrefaction process and its process stages involved are presented in Section 2.5 and reviews on torrefaction process are discussed in Section 2.6. Meanwhile, the effects of torrefaction temperature and torrefaction time on the properties of torrefied biomass are highlighted in Section 2.7. In addition, reviews on the mathematical models for torrefaction kinetic are presented in Section 2.8.

2.2 Malaysia Energy Scenario

A rapid growth population and economic development have affected the rising in demands of the energy consumption. Energy is a vital components to any economic activities and thus, adequacy of energy supply is very necessary (Ong et. al., 2011; Sulaiman et. al., 2011). Yusoff (2006) has reported that Malaysia's demand for energy is relatively high if compared to the developed countries such as Japan, Taiwan, and USA. Figure 2.1 indicates the energy demand in Malaysia from 1980 to 2010 and it was projected to further increase to 98.2 Mtoe (million tone of oil equivalent) by 2030 (Mohammed et al., 2011).

However, the energy sector in Malaysia is still dependent on the non-renewable fuels such as crude oil, natural gas and coal as the main source of energy (Ong et. al., 2011; Shuit et. al., 2009). Yusoff (2006) had also reported that in the year of 1999, the remaining reserves for the oil was 3.6 billion barrels and for the natural gas was 85.8 trillion standard cubic foot. Moreover, the natural gas reserves are expected to meet the country's demand only for the next 50-60 years while oil reserves are expected to last for the next 20 years only.

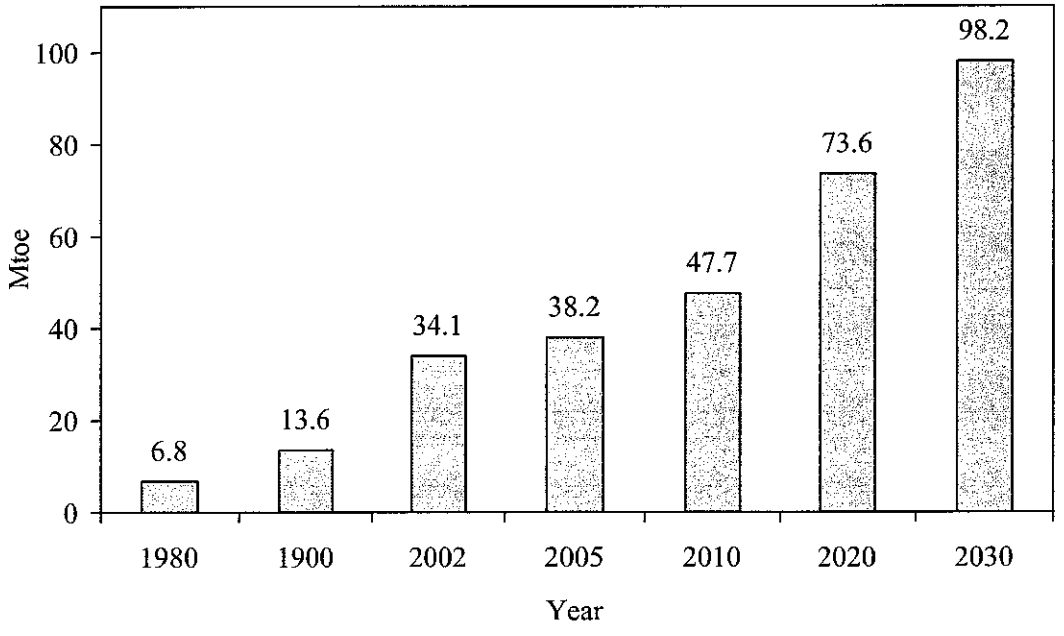


Figure 2.1 Energy demand in Malaysia (Mohammed et al., 2011).

Besides, the energy generation from the combustion of fossil fuel also threaten nature global ecosystem due to exhaust gas emission. The emission of greenhouse gases (GHG) and toxic gases such as carbon dioxide, nitrogen oxide and sulphur dioxide can cause global warming, climate change and acid rain (Shuit et. al., 2009; Ong et. al., 2011). Shuit et. al. (2009) had also reported that in 2005, about 93% of energy consumption in Malaysia has been generated from fossil fuels (natural gas, coal, diesel and oil) and only 0.5% of energy came from renewable sources such as biomass. It is a surprising fact and if this trend continued, Malaysia would suffer from lack of energy security. In order to meet the requirements in increasing demand of energy, protecting environment and ensuring energy security, Malaysia needs to develop and implement a more sustainable and eco-friendly energy supply.

2.3 Palm Oil

2.3.1 Overview of Malaysia Palm Oil Industry

Over the last 25 years, Malaysia palm oil industry has grown tremendously and Malaysia is now one of the largest producer and exporter of palm oil in the world. Initially, palm oil was introduced to Sumatera and Malaya area in the early 1900s. During the late 1950s, the expansion of the industry has started as part of government's diversified policy for agricultural products such as rubber and oil palm and to raise the socio-economic status of its population. (Sumathi et. al., 2008; Yusoff, 2006). Oil palm, also known as *Elaeis guineensis* belongs to the family of Palmae. The oil palm tree in Malaysia originated from West Africa. The first commercial palm oil estate in Malaysia was set up in 1917 at Tennamaran Estate, Selangor (Sumathi et. al., 2008). Shuit et. al. (2009) had reported that the rapid increase in the palm oil plantation area from 1975 to 2006 as shown in Figure 2.2. In the year of 2007, productive palm oil plantation area was 4.3 million hectares, with the increment of 3.4% as compared to 2006, which was 4.2 million hectares. In the year of 2010, the palm oil plantation was estimated to reach 4.7 million hectares and it was expected to increase up to 4.9 million hectares by 2012.

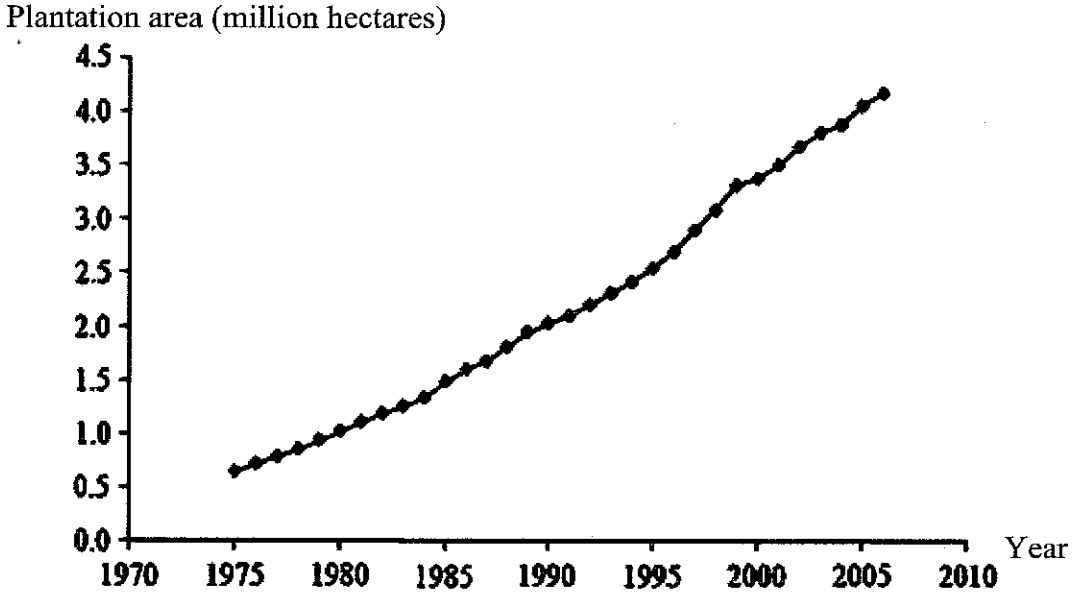


Figure 2.2 Plantation area of palm oil in Malaysia (Shuit et. al., 2009).

Due to the suitable climate and environment, palm oil becomes a major economic crop in Malaysia and Indonesia. In the world market, both Malaysia and Indonesia have accounted 90% of the palm oil world exporters. They have remained as the main exporter in the palm oil sector, accounting for 28.5 million tonnes (MnT) or 85% of the world's palm oil production as presented in Figure 2.3 (Sumathi et. al., 2008). In addition, it was forecasted that in the next 10 years, the demand will be higher due to the increasing of demands in the world total oil. Sumathi et. al. (2008) had also reported that the forecast production of palm oil for the year 2000 to 2020 for Malaysia and Indonesia as shown in Table 2.1.

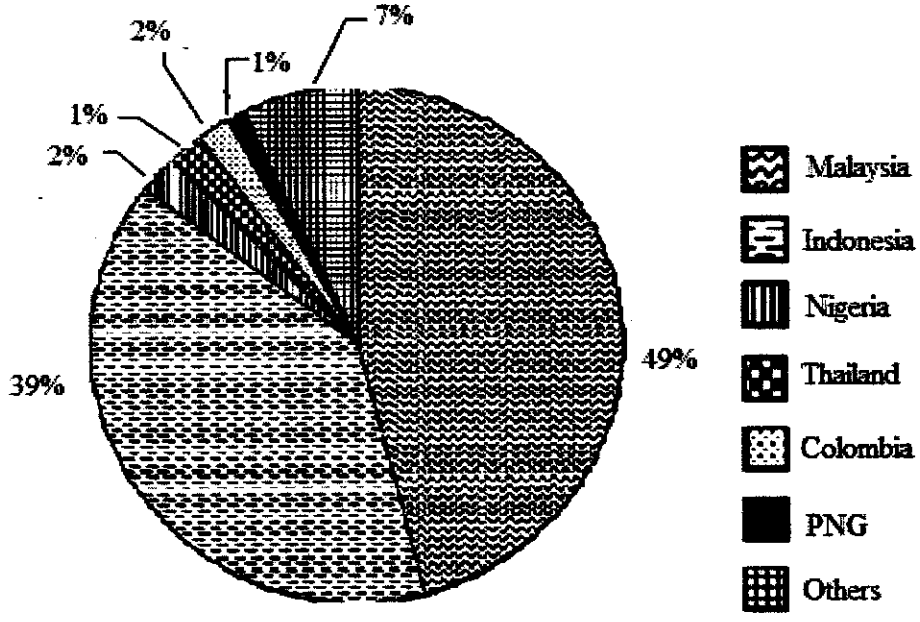


Figure 2.3 Palm oil exporters for world consumption in 2005 (Sumathi et. al., 2008).

In Malaysia, the palm oil production has increased due to an expansion of palm oil plantation area. The statistical analysis of palm oil production in Malaysia between the years of 2004 and 2009 was represented in Figure 2.4 (Mohammed et al., 2011). For example, they reported that in 2004, 12.1 MnT of palm oil has been produced in Malaysia. The palm oil production keep increasing for the next five years and it was estimated that 17.8 MnT of palm oil has been produced in 2009.

Table 2.1 Present and forecast palm oil production (MnT) at 2000-2020 (Sumathi et. al., 2008).

Year	Malaysia	Indonesia
Annual production		
2000	**10,100 (49.3%)**	**6700 (32.7%)**
2001	**10,700 (48.1%)**	**7720 (34.7%)**
2002	**10,980 (48.4%)**	**7815 (34.5%)**
2003	**11,050 (47.7%)**	**8000 (34.6%)**
2004	**10,900 (45.6%)**	**8700 (36.4%)**
2005	**11,700 (45.6%)**	**9400 (36.6%)**
Five-year averages		
1996–2000	**9022 (50.3%)**	**5445 (30.4%)**
2001–2005	**11,066 (47.0%)**	**8327 (35.4%)**
2006–2010	**12,700 (43.4%)**	**11,400 (39.0%)**
2011–2015	**14,100 (40.2%)**	**14,800 (42.2%)**
2016–2020	**15,400 (37.7%)**	**18,000 (44.1%)**

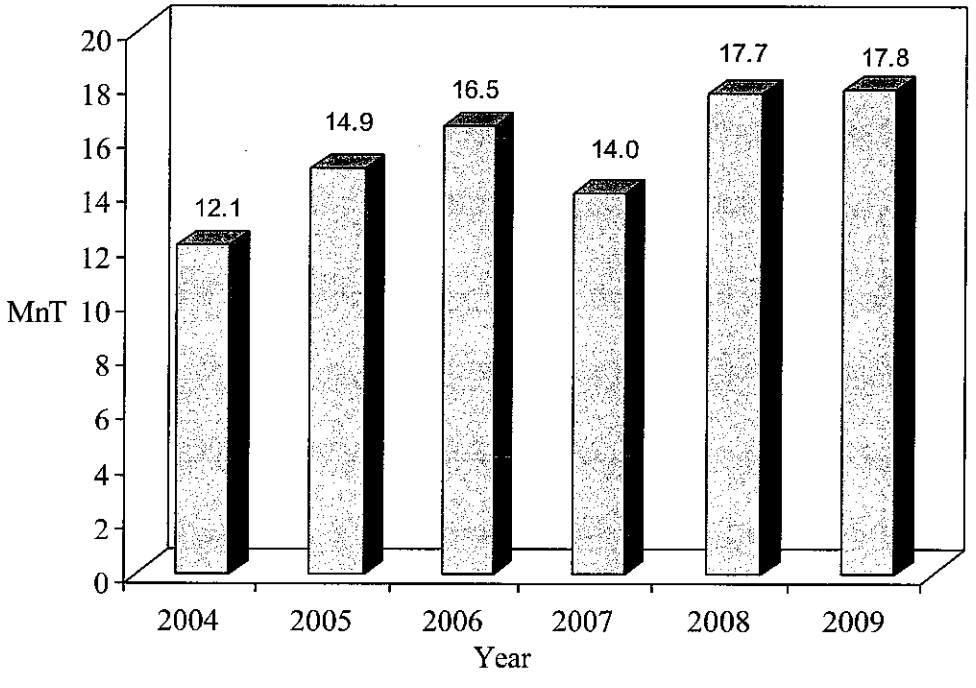
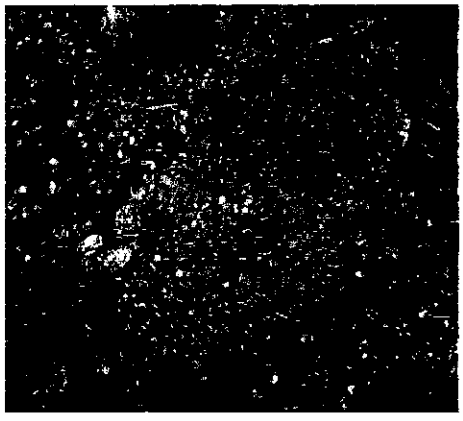


Figure 2.4 Palm oil production (MnT) in Malaysia from 2004 to 2009 (Mohammed et. al., 2011).

Geographically, Malaysia is blessed with favourable weather conditions where palm oil can be planted throughout the year. Palm oil trees are single-stemmed and the mature can grow up to 20 m tall. The leaves are pinnate and can reach between 3 to 5 m long (Yusoff, 2006). The fruit is reddish in colour which grows in large bunches. Normally, each bunch can have up to 200 individual fruits and weigh up to 30–40 kg. The fruit takes 5 to 6 months from the pollination to reach its maturity. The fruit comprises of an oily, fleshy outer layer (the pericarp), and a single seed (kernel), which is also rich in oil. Generally, the oil palms' fruit is usually harvested after 3 years from its planting. The maximum yield can be achieved in the 12–14th year, and then continuously declined until the end of the 25th year (Mohammed et. al., 2011; Sumathi et. al., 2008). For instance, Figure 2.5 shows the pictures of palm oil trees and its fresh fruit bunches.

(a) Palm oil trees

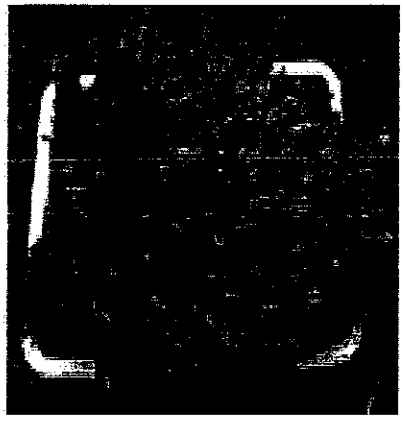


(b) Fresh fruit bunches (FFB)

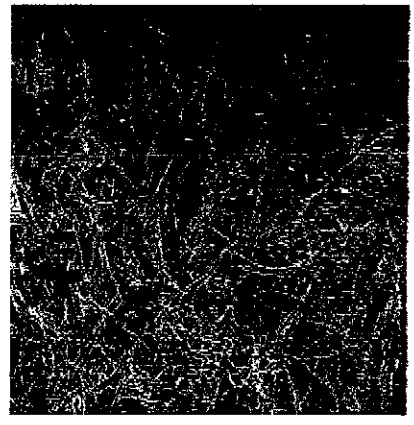
Figure 2.5 Palm oil trees and fresh fruit bunches (FFB).

2.3.2 Oil Palm Biomass

In line with the growth of palm oil production in Malaysia, the amount of biomass generated from palm oil mills were also increasing. The type of biomass produced from palm oil industry includes frond and trunk which from the trees, empty fruit bunches (EFB), fiber, shell, and kernel which from the fresh fruit bunches (FFB). Figure 2.6 shows the pictures of dried of EFB, mesocarp fiber and kernel shell. In order to illustrate the kinds of biomass produced, the simplified process flow of a palm oil mill is presented in Figure 2.7 (Sulaiman et. al., 2011).



(a) Empty Fruit Bunch (EFB)



(b) Mesocarp fiber

(c) Kernel shell

Figure 2.6 Dried of empty fruit bunch (EFB), mesocarp fiber and kernel shell.

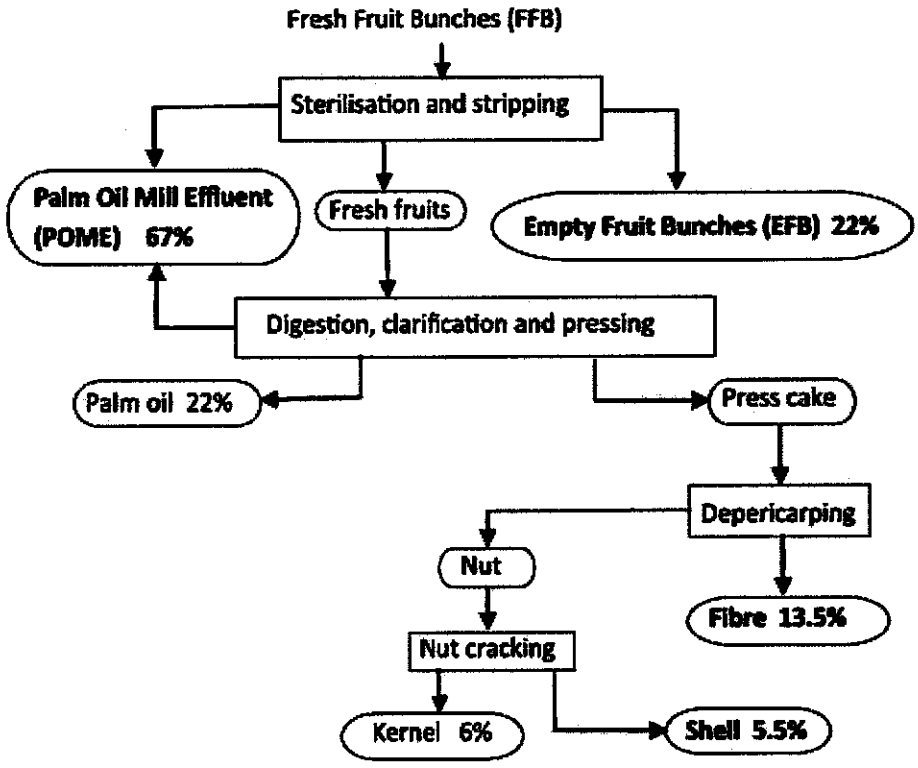


Figure 2.7 Simplified process flow of palm oil mill (Sulaiman et. al., 2011).

Furthermore, Mohammed et. al., (2011) had reported that one fresh fruit bunch contained 21% of oil, 23% of EFB, 14-15% of fiber, 6-7% of kernel and 6-7% shell. The major types of biomass produced from oil palm tree and the quantity produced per annum in million tonnes is illustrated in Figure 2.8. In general, one hectare of palm oil plantation can produce about 50-70 tonnes of biomass residues. Palm oil industry was produced the largest amount of biomass in Malaysia with 85.5% out of more than 70 million tonnes compared to others industries as shown in Figure 2.9 (Shuit et. al., 2009). The biomass that generated from wood, paddy and sugarcane plantation, municipal solid wastes were the other types of biomass produced. Other important issue for palm oil industry was to ensure the oil palm biomass is sustainable. The government had established Roundtable on Sustainable Palm Oil (RSPO) to ensure the sustainability of palm oil industry. RSPO has defined sustainable palm oil production as a legal, economically viable, environmentally, appropriate and socially beneficial management and operations (Shuit et. al., 2009). It was implemented through a policy which known as RSPO Principles and Criteria that was applicable to the management of palm oil plantations and palm oil mills.

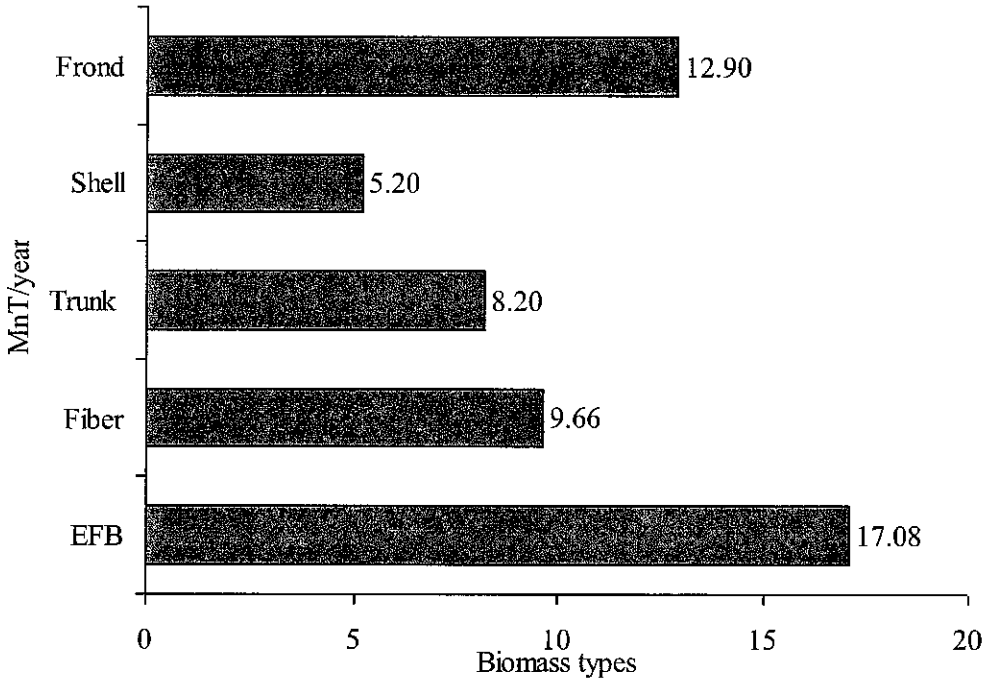


Figure 2.8 Types of oil palm biomass produced (MnT/year) in Malaysia at 2009 (Mohammed et. al., 2011).

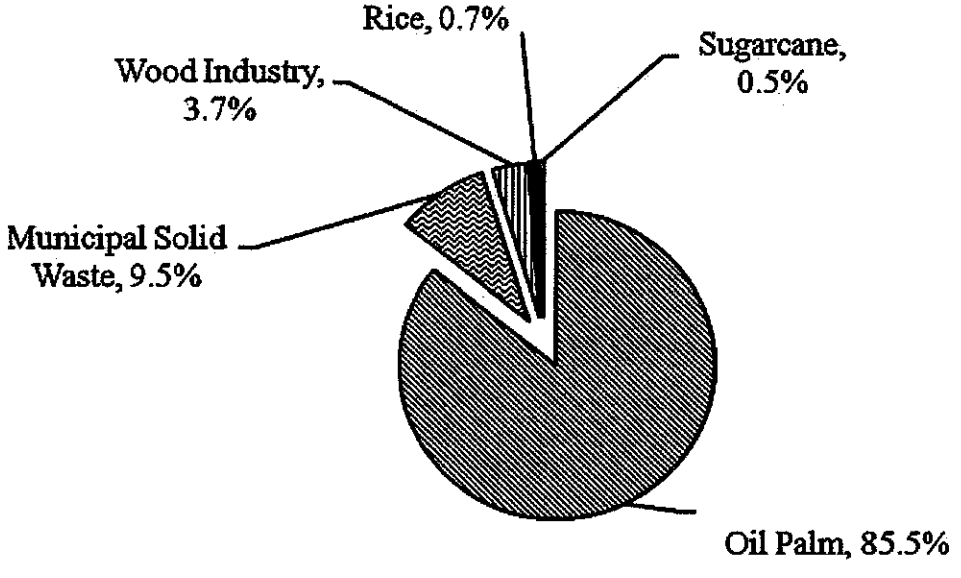


Figure 2.9 Biomass produced from different sources in Malaysia (Shuit et. al., 2009).

Moreover, each types of oil palm biomass have different chemical composition. The chemical properties of oil palm biomass varied according to their diverse origins and types of biomass. Mohammed et. al. (2011) had reported that the major chemical components of oil palm biomass were including cellulose, hemicellulose, lignin and ash as shown in Table 2.2. Among these biomass, the frond contained the highest cellulose content whereas the EFB contained the highest hemicellulose content compared to others biomass. They have also reported that the shell contained the highest lignin content.

Table 2.2 Chemical component of oil palm biomass (Mohammed et. al., 2011).

Components	Oil palm biomass (wt. %)				
	EFB	Frond	Fiber	Trunk	Shell
Hemicellulose	35.30	33.70	31.80	31.80	22.70
Cellulose	38.50	49.80	34.50	37.14	20.80
Lignin	22.10	20.50	25.70	22.30	50.70

2.4 Biomass Energy

Biomass energy is a renewable energy which has been attracting great attention these days. Due to serious environmental issues such as greenhouse effects and global warming from fossil fuel utilization, renewable fuel which derived from biomass is an essential (Chew and Doshi, 2011; Shuit et. al., 2009). According to Mohammed et. al. (2011), the energy that derived from biomass provides a clean energy situation which contributes an improvement in the environmental issues, economy and energy securities. Biomass is a very potential resource for energy generation because it is considered as 'carbon neutral' fuel and is a part of bio-cycle process (Zhang et. al., 2010; Deng et. al., 2009; Prins et. al., 2006a). Chew and Doshi (2011) have reported that during the biomass energy conversion processes, the released carbon dioxide will be re-captured by the re-growth of the biomass through photosynthesis process. Thus, biomass is a sustainable and low carbon fuel which offers the reduction in net carbon emissions to the environment as compared with the fossil fuel utilization.

Biomass is an abundant with sulphur and nitrogen negligible energy resource. Zhang et. al. (2010) have defined that the biomass as all the organic materials that produced from the photosynthesis process of the green plants. Meanwhile, Chew and Doshi (2011) have defined that the biomass as all the biological material derived from plant or animals as well as their waste and residues. Thus, it can be concluded that biomass is the materials that derived from living organisms, which includes plants, animals and their by-products. In addition, biomass also can be classified as woody biomass and non-woody biomass. The woody biomass comprises mainly of products and by-products which derived from the forest and trees sector. For non-woody biomass, it includes agricultural crops, agro-forestry residue, animal waste as well as tertiary waste (Chew and Doshi, 2011). Therefore, wide ranges of the biomass energies have been studied by many researchers around the globe, covered from the municipal solid wastes to agricultural wastes.

In general, biomass is composed of wide range organic materials such as hemicellulose, cellulose, lignin, lipids, proteins, and simple sugars. Among these organic materials, hemicellulose, cellulose and lignin are the main constituents in the biomass. Demirbas (2009) also had summarized the main component of biomass as shown in Figure 2.10. In term of elementary composition, biomass consisted of 51 wt.% of carbon, 42 wt.% of oxygen 5 wt.% of nitrogen of the biomass dry weight as reported by Zhang et. al. (2010). Besides, it also consisted trace amounts of hydrogen (0.9 wt.%) and chlorine (0.01–2 wt.%). Biomass energy can be defined as the solar energy stored in the form of chemical energy, which can be released when the chemical bonds of oxygen, carbon, and hydrogen molecules are broken by various thermo-chemical and biological processes (Chew and Doshi, 2011; Zhang et. al., 2010). Chen et. al. (2011a) and Arias et. al. (2008) have stated that diverse biomass energy conversion technologies have been developed which can be classified as the thermochemical processes such as combustion, gasification, pyrolysis and liquefaction; and the biological processes such as anaerobic digestion, fermentation, saccharification and esterification.

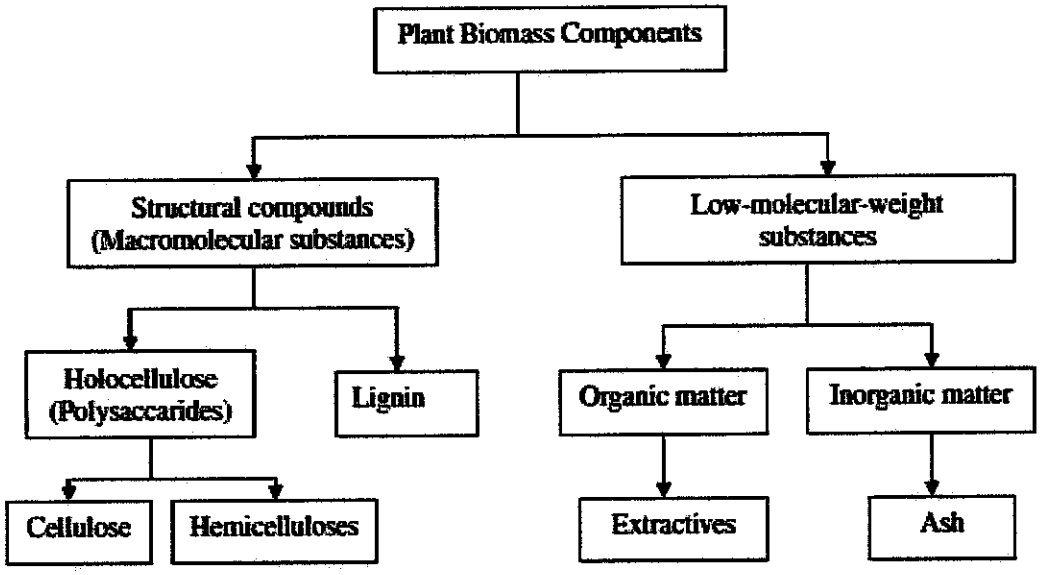


Figure 2.10 Main components in biomass (Demirbas, 2009).

Generally, biomass (woody and herbaceous) is made up of lignocellulose that consists of three main polymers namely hemicellulose, cellulose and lignin (Chen and Kuo, 2010a; Deng et. al., 2009; Prins et. al., 2006). Hendriks and Zeeman (2009) have stated that the hemicellulose is characterized as the linear polymers consisting of a variety complex carbohydrate structure of different polymers like pentose, hexose and sugar acids. It is usually substituted with other sugar side-chains to prevent the formation of crystalline structures. The dominant component of hemicellulose from hardwood and agricultural plants is xylan, while glucomannan for softwood. Besides, hemicellulose is also easy to be hydrolyzed into basic sugars. Other than that, hemicellulose also serves as a connection between the lignin and cellulose fibres which contribute to the rigidity of whole cellulose-hemicellulose-lignin network as represented in Figure 2.11 (Murphy and McCarthy, 2005).

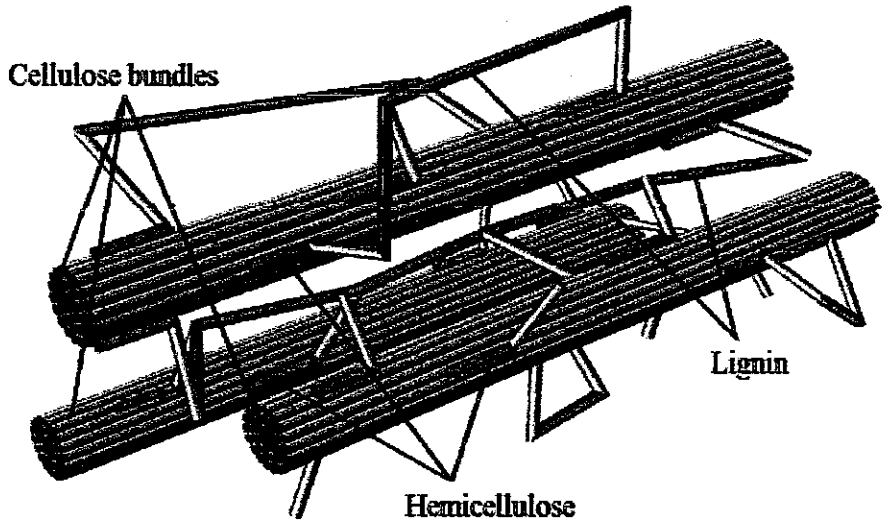


Figure 2.11 Arrangement of hemicellulose, cellulose and lignin in biomass (Murphy and McCarthy, 2005).

The cellulose exists of *D*-glucose subunits, linked by β-1, 4 glycosidic bonds. Cellulose in a plant consists of parts with a crystalline structure and some part of it is amorphous structure. The cellulose strains are 'bundled' together and also known as cellulose bundles. These cellulose bundles are mostly independent and weakly bound through hydrogen bonding (Mohammed et. al., 2011). Therefore, the chain is more stable and resistant to chemical attack. Lignin is one of the most abundant polymers in nature and is present in the cellular wall. It is characterized as highly branched polyphenolic constituents. Hendriks and Zeeman (2009) have stated that the main function of lignin is to give the plant structural support, resistance against microbial attack and oxidative stress. According to Chen and Kuo (2010a), thermal decomposition of hemicellulose occurs at temperatures ranging from 150 to 350 °C, whereas cellulose is decomposed at the temperature of 275 to 350 °C. The lignin is featured by gradual decomposition from the temperatures between 250 to 500 °C.

2.4.1 Issues Faced with Biomass Utilization

Currently, biomass are not fully utilized, with only a small fraction is used for the energy generation. Biomass, like other energy resource has its own advantages and disadvantages. According to Zhang et. al. (2010), as compared the biomass with the fossil fuel such as coal, biomass contains higher volatile matter.

Typically, biomass contains 80% of volatile matter whereas contains 20% of volatile matter in fossil fuel. Therefore, biomass has better ignition stability and can be easily processed thermo-chemically into gas fuels such as hydrogen. Besides, higher volatile matter in biomass also resulting in less char produced during utilization. This aspect is important especially during gasification process to maximize the gas products (Prins et. al., 2006a). Moreover, the reactivity of biomass is higher than that of coal, so that the burning time taken for biomass is less than coal.

However, biomass have also undesirable properties which contributed as the disadvantages in the fuel production. Zhang et. al. (2010) had reported that in comparison to fossil fuel, biomass have lower heating values. For example, the heating value for agriculture residues and woody materials are 15-17 GJ/t and 18-19 GJ/t, respectively, whereas that of coal is 20-30 GJ/t. These might be related to the high moisture and high oxygen contents (Uemura et al., 2011; Deng et. al., 2009; Bridgeman et. al., 2008; Prins et. al., 2006a). The heating value of the biomass is negatively correlated with the moisture content as shown in Figure 2.12. From the graph, as the moisture content increases, both high heating value (HHV) and low heating value (LHV) of the biomass decreases.

Generally, HHV and LHV are used to describe the heat production of a unit quantity of fuel during its complete combustion process (Uemura et al., 2011). As the HHV is incorporated with the heat of the condensation of the water vapour during the combustion, the curve of the HHV is always above than the LHV. Besides the relation high moisture content with heating value, high moisture content also can contribute for storage complication such as biodegradation and self heating (Chew and Doshi, 2011; Arias et. al., 2008; Bridgeman et. al., 2008). Thus, the raw biomass cannot be stored for a long time and encountered challenges when handling the raw biomass in the fuel applications.

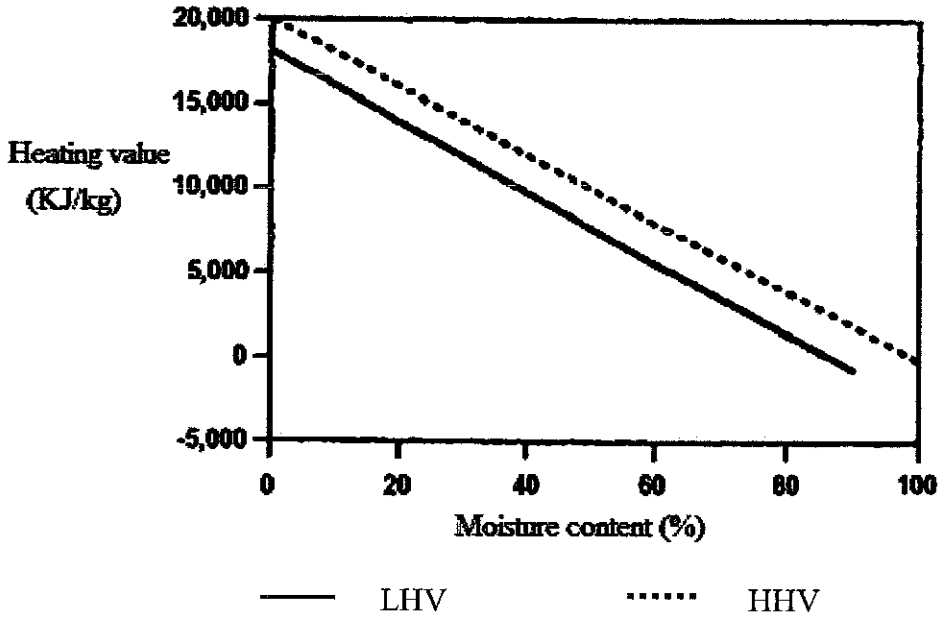


Figure 2.12 Relationship between heating value and moisture content of biomass fuel (Zhang et. al., 2010).

Moreover, biomass fuels are known for their elevated oxygen content. Typically, the oxygen content is high which can reach up to 35 wt.% of the raw biomass. In comparison, the oxygen content of biomass is approximately ten times higher than that of a high-rank coal, which is below than 4 wt.% (Zhang et. al., 2010). The high amount of oxygen is also associated with the heavy smoking occurrence during the biomass utilization (van der Stelt et. al, 2011). In addition, Prins et. al. (2006a) had reported that although wood is a clean fuel with low nitrogen and sulphur content, some problem may occur during gasification process including the formation of condensable tars in gasifiers. It gave problems to the equipment such as choking and blockage of piping. In addition, woods have high O/C ratio as compared with the O/C ratio of fossil fuel such as coal. Hence, it can contribute in lower efficiency during the gasification process.

Zhang et. al. (2010) had also reported that others typical issues associated with the biomass combustion were fouling and corrosion in the combustor. It can lead to the reduction of the heat transfer in the combustor. Commonly, fouling was associated with the composition of biomass ash. It contained alkali metals and some other elements in trace amounts such as silicon, sulphur, chlorine, calcium and iron.

For example, herbaceous biomass such as straws and grass contain higher contents of alkali, sulphur and chlorine. During biomass combustion, the chemical reactions of these elements reacted occurred. They can be deposited in the forms of chlorides, silicates or sulphates on the wall of the combustor or the surface of the heat transfer elements. The ash deposition also contributed to the corrosion in the process equipment. Another issue related to the utilization of biomass is grindability. Arias et. al. (2008) had reported that the biomass is difficult to grind due to its tenacious and fibrous nature which makes it is difficult to reduce biomass into small homogenous particles. Hence, it leads to poor grindability and difficulty in the process control (van der Stelt et. al, 2011). These problems have serious consequence especially when this biomass is to be used in the pulverised systems such as co-firing with coal and in the entrained flow gasifier (Deng et. al., 2009; Bridgeman et. al., 2008).

2.4.2 Pretreatment Technologies for Biomass

When biomass is consumed as feedstock or solid fuel, the outmost importance is how to utilize it efficiently. Thus, various number of pretreatment methods of biomass have been employed by researchers to ensure that their use as energy source is environmental friendly and economically efficient. It was known that the lignocellulosic biomass is featured as a strong tenacious structure and composed of densely packed layers of hemicellulose, cellulose and lignin. The pretreatment methods are required to upgrade and modify the chemical and physical properties of biomass. Moreover, Almeida et. al. (2010) had stated that the modification is required to improve energy concentration and homogeneity of the biomass during energy conversion processes. The pretreatment methods that commonly applied by the researchers including the dewatering and drying, pulverization or size reduction, pelletization and dilute acid pretreatment as illustrated in Figure 2.13 (Chen et. al., 2011a; Chen et. al., 2011c).

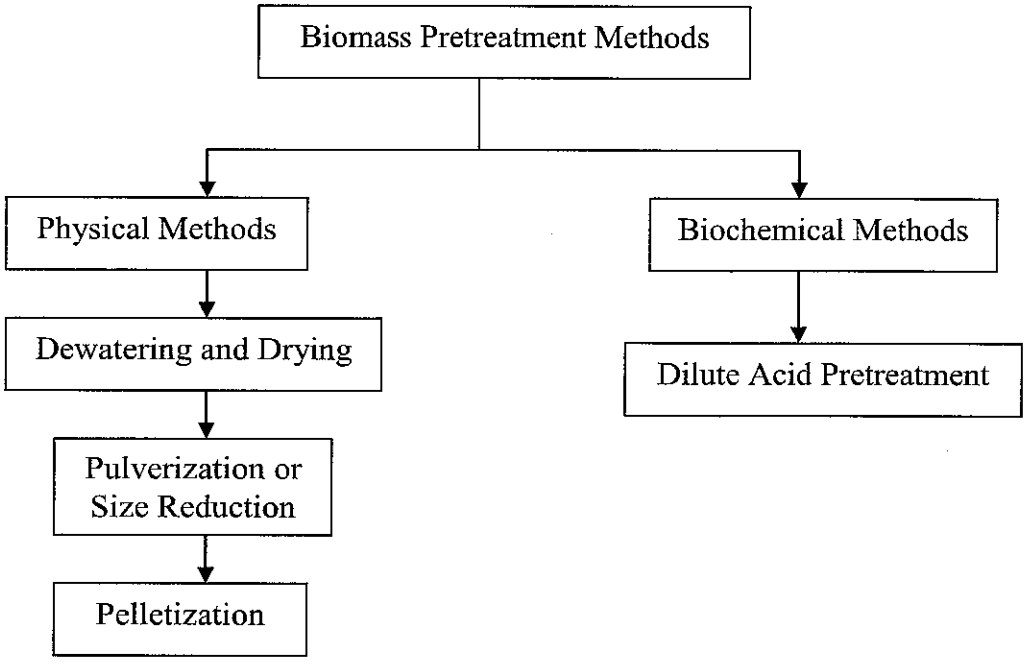


Figure 2.13 Biomass pretreatment methods (Chen et. al., 2011a; Chen et. al., 2011c).

One of the common approaches to the upgrading of biomass is dewatering and drying. Generally, it is a physical pretreatment method that reduces the moisture content in the biomass. Consequently, the method can reduce microbial activity, increase the calorific value and improve the volumetric energy density of biomass. Besides that, the combustion efficiency of biomass will be enhanced. However, sometimes dewatering and drying of biomass is not sufficient enough due to their poor durability when barely exposed to humid environment such as condensed water or snow. It can regain moisture, might be rotten and decomposed during storage. Thus, the biomass needs to be stored in a dry and possibly, in the conditioned and controlled environment (Bergman, 2005a; Chen et. al., 2011a).

Pulverization is important to improve the physical properties of biomass where the tenacious nature structure turns into brittle. Moreover, pulverization is also known as size reduction greatly enlarges the surface per unit mass of biomass. By providing larger surface area, it is conducive for the reaction taking place during biomass utilization such as combustion, gasification or pyrolysis. Besides, because of the biomass had been grinded into powder form, it can be blended with coal to serve as a pulverized fuel in the boilers and blast furnaces.

However, very small particle size ranges of some types of the pulverized biomass can cause agglomeration in the reactor (Chen et. al., 2011b). It can lead to low flowability and poor fluidization behaviour of the pulverized biomass during utilization. Therefore, particular handling of the pulverized biomass such as the suitable particle sizes and shapes, dispersion of the powder need to be improved. Thereby, it can facilitate the injection of biomass powder during the utilization.

Pelletization can be defined as drying and pressing of biomass under high pressure to produce cylindrical pieces of compressed and extruded biomass. The temperature and pressure are considered as the main parameters in pelletization. The pellet production is performs at the temperature of 150 ^{o}C which required only small particle size of feedstock with the maximum size of 3-20 mm and moisture content below 10-15% which (Uslu et. al., 2008). Biomass pellet has offered attractive properties such as easy to comminute into small particles, resistant to moisture uptake and microbiological decay (Bergman, 2005a). It is also highlighted that the biomass pellet has enabled transportation over long distances and seasonal storage (Chen et. al., 2011a; Bergman, 2005a). Another advantage of pelletization is enabled the free flowing which improved the rate of flow control in the reactor design as reported by Uslu et. al. (2008).

Others approach is dilute acid pretreatment method which had been used to convert lignocellulosic biomass such as sugarcane bagasse in the bioethanol production (Chen et. al., 2011c; Rahman et. al., 2006). According to Chen and Kuo (2011b), the main functions of dilute acid pretreatment are to convert hemicellulose contained in lignocellulosic biomass to soluble sugars and facilitate the subsequent enzymatic hydrolysis of cellulose. The process can be carried out in a high temperature environment using conventional heating or microwave heating (Chen et. al., 2011d). An efficient pretreatment process is crucial in order to improve the rate of enzymatic hydrolysis and thus, increase the yield of fermentable sugars (Chen et. al., 2011c). It was reported that during hydrolysis process, the acid concentration is an important parameter for releasing of sugars such as xylose and glucose whereas temperature is responsible for the decomposition of sugar to various by-products such as acetic acid and furfural (Rahman et. al., 2006).

Chen et. al. (2011c) had also proposed two steps dilute sulphuric acid pretreatment method. The first step is performed under low severity to give high recovery of the hemicellulose-derived sugar in liquid. Meanwhile, in the second step, it is carried out under greater severity to allow the cellulose is more accessible to enzymatic attack.

2.5 Torrefaction Process

2.5.1 Definition and its Advantages

Other than the aforementioned pretreatment methods, there is one recommended method to improve the raw biomass properties as a fuel which is a torrefaction process. Torrefaction process is one of the pretreatment for improving the physiochemical properties biomass. It is a heat treatment process that carry out under atmospheric condition in the absence of oxygen in the low temperature ranges between 200 to 300 °C (Chen et. al., 2011a; Deng et. al., 2009; Chen and Kuo, 2010a; Bridgeman et. al., 2008). It is also commonly known as roasting, mild pyrolysis, high temperature drying and thermal pretreatment (Chew and Doshi, 2011; van der Stelt et. al, 2011). According to Prins et. al. (2006a) and Prins et. al. (2006c), the products of torrefaction consisted of dark colour solid which retained at least 80% of energy content of feedstock; condensable liquid including acetic acid, acetaldehyde, formic acid, methanol and acetone; and non-condensable gases which were mainly CO_2, CO and small amounts of CH_4 and H_2. Chen and Kuo (2010a) have also reported that the torrefaction process strongly dependent on the composition and decomposition temperatures of the lignocellulosic constituents in the biomass namely hemicellulose, cellulose and lignin.

Torrefaction process modified the physiochemical properties of biomass such as decreased the mechanical property which improved the friability and grindability; increased the homogeneity which enhanced the ignitibility and reactivity during gasification; produced hydrophobic solid product with higher energy density and calorific value (Chew and Doshi, 2011; Uemura et. al., 2011; Deng et. al., 2009). In addition, torrefied biomass has lower moisture content and higher heating value as compared with the raw biomass (Deng et. al., 2009; Bridgeman et. al., 2008).

The lower moisture content can prevent fungal attack and biodegradation. Therefore, torrefaction increased the storage duration and reduced handling cost of the raw biomass. Moreover, torrefaction process also removed the low weight organic volatile components and depolymerised the long polysaccharide chains, producing a hydrophobic solid product as reported by Prins et. al. (2006b). Thus, it had increased the carbon content, heating value and energy density of the torrefied biomass.

Furthermore, the tenacious and fibrous nature of biomass became more brittle after torrefaction process. This improved the grindability of the biomass and made it easier to process this biomass into smaller homogenous particles (Arias et. al., 2008). Thus, it can reduce the cost of grinding or milling process of the biomass. Moreover, the homogenous particles of the torrefied biomass can be used in the pulverised systems, such as co-firing with coal in the boilers and gasification in the entrained flow gasifier (Deng et. al., 2009; Bridgeman et. al., 2008). According to Bridgeman et. al. (2008), the modified fuel can be compacted into high grade pellets with superior characteristics as compared with the standard wood pellets. The process can be incorporated by combining the drying, torrefaction and pelletisation process (TOP). They have also reported that TOP contributed to the energy efficiency and economic benefit. Finally, the torrefied biomass had become suitable feedstock for the entrained flow gasification, which previously the raw biomass was not considered feasible. It was because the torrefied biomass form became more spherical shaped particles during the grinding process (Bergman et. al., 2005b).

2.5.2 Process Stages

When the biomass was fed into TGA or tube furnace, it had passed several stages that can be differentiated based on the time-temperature characteristics. The time-temperature characteristics of the torrefaction process are illustrated in Figure 2.14. It was very important to define the time-temperature characteristics to provide understanding in the process stages that involved during torrefaction process.

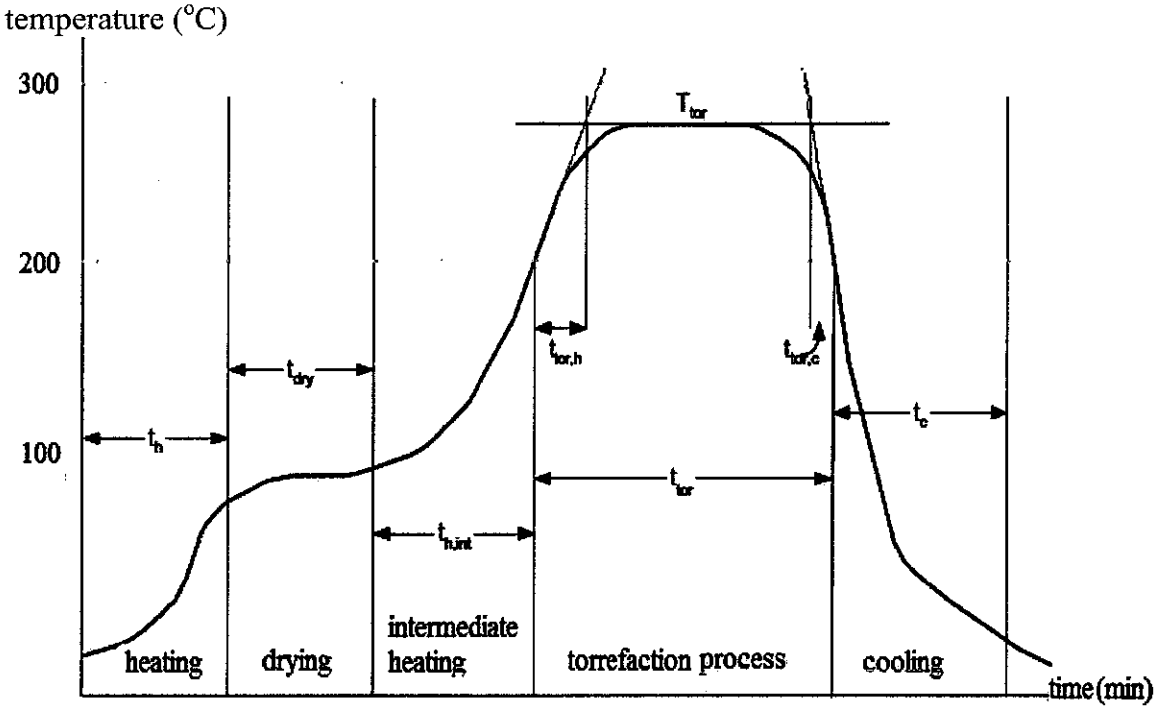


Figure 2.14 Temperature-time characteristics in torrefaction process (Bergman et. al., 2005a).

In general, torrefaction temperature was in the range of 200 to 300 °C. Through this temperature ranges, torrefaction process is divided into several stages, such as initial heating, drying, intermediate heating, torrefaction and cooling (van der Stelt et. al., 2011; Bergman et. al., 2005a). When biomass was fed into a torrefaction reactor, it was heated from ambient temperature until the stage of drying is reached at temperature around 105 °C. At this stage, temperature is kept constant, while the moisture was started to evaporate. Once the stage was completed, temperature was increased and had been considered as the intermediate heating stage. During this stage, the mass loss occurred caused by the dissociation of the light fraction of hydrocarbons and an evolution gases.

The temperature was further increased until the desired torrefaction temperature was reached. By definition, torrefaction process started when the temperature reached to 200 °C and the maximum temperature was 300 °C. The process ended when the system was cooled down from the selected temperature to 200 °C again.

In this temperature ranges, it can be divided into three time-temperature phases. Firstly, the biomass was heated from 200 °C to the desired torrefaction temperature, T_{tor} in a specific period, $t_{tor,h}$. Then, the temperature was maintained for period of T_{tor}. During T_{tor}, torrefaction process was at its peak where the decomposition reaction is the main reaction. The reaction time of torrefaction can be defined as the sum of $t_{tor,h} + T_{tor}$. In contrast to the cooling period, the solid product was more thermally stable as the highest reactive parts have already reacted. Therefore, it was expected that the decomposition reactions was stopped as soon as the temperature was decreased (Bergman et. al., 2005a).

During torrefaction process, biomass was thermally decomposed and various types of volatile resulting in loss of mass and chemical energy. During this period, most of the loss of mass torrefied biomass occurred. The mass and energy yields of the torrefied biomass were strongly dependent on the temperature, reaction time and biomass types as well as the composition of hemicellulose, cellulose and lignin in the biomass. Besides, hemicellulose, cellulose and lignin were behaved differently when subjected to high temperature environment. In the temperature ranges of 200 to 300 °C, hemicellulose was the most reactive fraction. Below 250 °C, hemicellulose was subjected to limited devolatilisation and carbonisation but above 250 °C, it was subjected to extensive devolatilisation and carbonisation. In comparison with hemicellulose, cellulose is more thermo-stable and only limited devolatilization and carbonization at 200 to 300 °C. Meanwhile, the reactivity of lignin was the lowest when compared to hemicellulose and cellulose (Bergman et. al., 2005a).

2.6 Reviews on Torrefaction Process

In the last few decades, it have been reported that torrefaction was the recommended process to enhance the physiochemical properties of biomass. There were variety publications and information about the torrefaction of biomass in the open literatures. All around the world, numerous torrefaction studies were done on diverse biomass resources such as oil palm wastes (Uemura et. al, 2011); eucalyptus (Almeida et. al., 2010; Arias et. al., 2008); reed canary grass, wheat straw and willow (Bridgeman et. al., 2008); and larch, willow and beech (Prins et. al., 2006a).

Furthermore, torrefaction studies on wood dusts have been conducted by Uslu et. al. (2008), on bamboo, willow, coconut shell and wood (*Ficus benjamina L.*) by Chen and Kuo (2010a), spruce and beech wood by Repellin et. al. (2010) and rice straw and rape stalk by Deng et. al. (2009). These evidences showed that torrefaction process is becoming an important pretreatment method for biomass and it is still required a lot of fundamental studies for better understanding of this process.

Van der Stelt et. al. (2011) had reported that the researches focused on torrefaction process have been started in France in the 1930s, but the publications about this area were quite limited during that period. One of the significant earlier works of torrefaction process was pioneered by Bourgois and Doat in the 1980s. They have reported that torrefaction at temperature of 270-275 °C successfully had increased the lower heating value from 18.6 to 22.7 MJ/kg for eucalyptus and 17.9 to 21.5 MJ/ kg for a mixture of chestnut and oak (Prins et. al., 2006c). Another significant work of torrefaction was conducted by Pentananunt et. al. at the Asian Institute of Technology in Bangkok on 1990. They have studied the combustion characteristics of torrefied wood in a bench scale torrefaction unit. They have compared combustion characteristics of torrefied wood produced after 2-3 hours of torrefaction. They have found that the torrefied wood had significantly higher combustion rate and produces less smoke than wood (Van der Stelt et. al., 2011).

Since 2002, one of the important research centres that actively involved in the torrefaction is Energy research Centre Netherlands (ECN). Their research focused on the fundamental of torrefaction process on variety of woody biomass and herbaceous species such as straw and grass (Bergman et. al., 2005a; Bergman et. al., 2005b; Bergman et. al., 2005c). In particular, they have studied on the influence of feed, particle size, torrefaction temperature and reaction time. The torrefied biomass properties such as the mass and energy yields of the solid, liquid and gases products have been investigated by Bergman et. al. (2005a). The basis of the principles of torrefaction it is strongly believed that it is has high potential to become a leading biomass pretreatment technology. Thus, this centre served as the catalyst research on torrefaction process and most of their findings were used by the researchers to develop the torrefaction process technology throughout the world.

Furthermore, thermodynamic analysis of biomass gasification coupled with torrefaction had been performed (Prins et. al., 2006a; Prins et. al., 2006b; Prins et. al., 2006c). This work was also in line with the previous works that had been done by the Energy research Centre Netherlands (Bergman et. al., 2005a; Bergman et. al., 2005b). Prins et. al. (2006b) had also conducted research that focused on the weight loss kinetics of wood torrefaction. They reported that the weight loss kinetics for torrefaction of willow can be described by a two-step reaction in series model. The fast initial step may be representative for hemicellulose decomposition, whereas the slower subsequent reaction represents cellulose decomposition and secondary charring of hemicellulose fractions. Meanwhile, Prins et. al. (2006c) had reported the analysis products of torrefied larch, straw, beech and willow. The studies had showed that the beech, willow and straw were found to produce more volatiles than larch, especially more methanol and acetic acid. At torrefaction temperature of 270 °C with reaction time of 15 min, the increased in energy density of the solid product was much higher for deciduous wood than for coniferous wood; 17% versus 7%. Besides, torrefaction of deciduous wood at these conditions still retained 90% of the energy in the solid material.

The impact of torrefaction on the production of syngas from wood gasification in an entrained flow reactor was evaluated by Couhert et. al. (2009). Due to torrefaction decreased the O/C ratio of the biomass, they have showed that the quantity of the produced syngas increased with the severity of the torrefaction. Deng et. al. (2009) had evaluated the properties of torrefied rice straw and rape stalk for co-gasification. They have reported that the heating values of the torrefied rice straw and rape stalk increased up to 17 % and 15 % as compared with raw materials. The properties of the torrefied agricultural residues were closer to that of coal; therefore, torrefaction was a promising method to combine with coal co-gasification. Arias et al. (2008) had studied that torrefaction process gave the significant impact on the grindability and reactivity of wood biomass when used in pulverized systems. They found that after the torrefaction of eucalyptus at 240 °C for torrefaction time of 30 min, the grinding characteristics of the biomass were apparently improved.

Bridgeman et. al. (2008) had been studied on torrefaction of the reed canary grass, short rotation willow coppice and wheat straw. Their work focused on the chemical analysis (C, H, N, O, ash) and the combustion behaviours of the raw and torrefied biomass by differential thermal analysis (DTA). They havr showed that torrefied fuel can contain up to 96% of the original energy content of raw biomass on mass basis. Besides, they have showed that both volatile and char combustion of the torrefied fuel become more exothermic compared with raw biomass and the degree of exothermic level was dependant on the severity of the torrefaction process. They also had showed that the torrefied biomass ignited more quickly under exposure of methane-air flame, due to its low moisture content and resulting faster heat transfer process. In addition, Almeida et. al. (2010) had studied three eucalyptus wood species at different torrefaction conditions in order to investigate alteration of structural and energy properties. The most severe condition which were at 280 °C with torrefaction time of 5 hours had caused mass loss more than 35%, increased 27% of energy content and severe damage to the anatomical structure. Their work have also showed that torrefaction always resulting in high energy yield compared to that of mass yield. Thus, the main benefit of torrefaction was to concentrate biomass energy compared to the raw biomass. They have also suggested that the mass loss as a relevant indicator to determine the effects of temperature and duration of torrefaction process.

Chen and Kuo (2010a) have also investigated torrefaction of bamboo, willow, coconut shell and wood (*Ficus benjamina L.)* by using thermogravimetric analysis (TGA). Their studies have emphasized on the impact of torrefaction on hemicellulose, cellulose and lignin content in the biomass. They have conducted two different torrefaction which were consisting of light torrefaction at 240 °C and severe torrefaction at 275 °C. They have reported that hemicellulose was severely decomposed at light torrefaction whereas cellulose was more resistant toward light torrefaction. However, at severe torrefaction, the cellulose and lignin were severely decomposed. Once severe torrefaction performed, the effect on decomposition of cellulose was more severe, especially for the bamboo and willow. They have also suggested that suitable condition for producing fuel with higher energy density was less than 1 hour under light torrefaction.

2.7 Effects of Torrefaction Temperature and Torrefaction Time to the Properties of Torrefied Biomass

2.7.1 High heating Value, Ultimate and Proximate Analysis

In the early years, the studies on torrefaction were mainly focused on wood based materials. Recently, the studies on diverse biomass including the agricultural crops and agro-forestry have been investigated. Table 2.3 summarized the properties of various raw biomass for ultimate, proximate analysis and high heating value.

Table 2.3 Ultimate, proximate analysis and high heating value (HHV) of different types of raw biomass (Chew and Doshi, 2011).

Biomass	Ultimate analysis (wt.%)				Proximate analysis (wt.%)			HHV (MJ/ kg)
	C	H	N	O	VM	FC	A	
Woody biomass								
Banyan	46.20	6.08	0.08	46.53	77.57	18.03	1.11	20.29
Beech	47.20	6.00	0.40	45.20	84.20	15.50	0.30	18.30
Birch	45.50	6.20	0.10	48.20	-	-	-	16.44
Eucalyptus	49.00	6.10	0.20	44.60	-	-	-	19.40
Larch	48.80	6.10	0.10	44.90	82.80	-	0.10	19.50
Lauan wood	48.77	6.77	0.10	44.36	75.08	17.22	-	20.41
Pine wood chip	47.21	6.64	0.17	45.76	85.98	13.76	0.27	18.79
Sawdust	40.85	6.17	0.03	39.07	73.15	13.02	0.38	-
Willow	47.20	6.10	0.34	44.80	87.60	10.70	1.70	19.00
Non-woody biomass								
Baggase (sugarcane)	44.80	5.80	0.25	49.10	67.31	-	1.53	15.50
Bamboo	43.84	6.05	0.07	46.53	73.56	19.94	3.51	18.70
Cotton stalk	46.43	6.18	0.80	42.62	76.92	19.19	2.70	-
Empty fruit bunches	45.53	5.46	0.45	43.40	-	-	-	17.70
Kernel shell	46.68	5.86	1.01	42.01	-	-	-	19.78
Mesocarp	46.92	5.89	1.12	42.66	-	-	-	19.61
Reed canary grass	48.60	6.80	0.30	37.30	82.50	12.10	5.50	19.50
Rice straw	39.00	5.08	1.03	40.96	68.83	17.46	8.59	17.12
Wheat straw	47.30	6.80	0.80	37.70	76.40	17.30	6.30	18.90

*C: carbon; H: hydrogen; N: nitrogen; O: oxygen; VW: volatile matter; FC: fixed carbon; A: ash; HHV: higher heating value

As shown in Table 2.3, these raw biomass have different composition of carbon, hydrogen, nitrogen, oxygen and HHV. In general, ultimate analysis revealed that raw biomass was composed of 40-50% of carbon, 35-45% of oxygen, about 5-6% of hydrogen, 0-1.5% of nitrogen and negligible amount of sulphur. Proximate analysis had showed that about 75-87% of raw biomass was made up of volatile matter, 15 to 20% of fixed carbon and the rest was ash content. The typical value for HHV of raw biomass was in the range of 15-20 MJ/kg.

In addition, the ultimate analysis of torrefied biomass was shown in Table 2.4. In comparison with the raw biomass, the torrefied biomass had 50-65% of carbon and 20 to 45% of oxygen. The carbon content increased with the increasing of torrefaction temperature, whilst hydrogen and oxygen content decreased. After torrefaction, the increased in carbon and decreased in oxygen content had reduced the O/C ratio for these biomass. The increased in carbon content attributed to the increased in the high heating value of the torrefied biomass. During torrefaction process, the reactions occurred had liberated the compounds contained higher proportions of hydrogen and oxygen such as CO, CO_2, CH_4, H_2 and water, thus reduced the relative concentration of these elements in the torrefied biomass (Bridgeman et. al., 2008).

Moreover, a graphical illustration had been used to study the elemental changes of torrefied biomass which was the van Krevelen diagram. In this diagram, hydrogen to carbon ratio was plotted against the oxygen to carbon ratio. Figure 2.15 illustrates the atomic ratio of coal sample and untreated biomass whereas Figure 2.16 illustrates the ratio of coal sample and torrefied biomass above 250 °C. In this diagram, the dotted straight lines represented the dehydration reaction pathway. Prior to torrefaction, the woody biomass sample have the H/C ratio of 1.6 and O/C ratio of 0.75. At the torrefaction temperature above than 250 °C, the van Krevelen diagram had shown that the elemental ratios of biomass shifted to coal as presented in Figure 2.16. By comparing these two figures, it can be clearly seen that the torrefied biomass had lower of O/C ratio and H/C ratio and torrefaction process shifted the elemental ratios of biomass towards coal.

Table 2.4 Ultimate analysis of different biomass for torrefaction duration of 0.5 h and 1.0 h (Chew and Doshi, 2011).

Biomass	*t* (h)	*T* (° C)	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)
Woody biomass						
Banyan	1.0	230	53.55	6.84	0.15	37.08
	1.0	260	60.73	6.46	0.18	28.52
	1.0	290	66.21	6.22	0.15	22.57
Beech	1.0	240	51.70	5.40	-	42.90
	1.0	260	54.40	5.20	-	40.40
Eucalyptus	0.5	240	53.10	6.10	0.10	40.60
	0.5	260	55.70	5.80	0.10	38.30
	0.5	280	57.80	5.50	0.20	35.30
Lauan wood	1.0	220	54.91	6.85	0.17	38.07
	1.0	250	65.37	6.06	0.16	28.41
	1.0	280	65.76	5.47	0.16	28.61
Willow	1.0	230	56.59	6.41	0.14	34.21
	1.0	260	65.16	7.10	0.23	24.33
	1.0	290	67.55	7.06	0.22	20.92
Non-woody biomass						
Baggase (sugarcane)	1.0	230	48.60	5.60	0.25	45.50
	1.0	250	50.60	5.60	0.30	43.50
	1.0	280	52.80	5.30	0.39	41.50
Bamboo	1.0	230	56.68	6.18	0.17	32.42
	1.0	260	62.26	6.29	0.13	24.64
	1.0	290	64.58	6.56	0.16	19.31
Empty fruit bunches	1.0	220	46.75	4.68	1.27	41.42
(oil palm)	1.0	250	47.07	4.95	1.35	42.24
	1.0	300	49.56	4.38	1.27	43.19
Kernel shell	1.0	220	45.87	6.31	0.40	43.07
(oil palm)	1.0	250	51.89	5.71	0.47	38.50
	1.0	300	54.21	5.08	0.50	36.66
Reed canary grass	0.5	230	49.30	6.50	0.10	-
	0.5	250	50.30	6.30	-	37.00
	0.5	270	52.20	6.00	0.10	37.30

* t: time; T: temperature; C: carbon; H: hydrogen; N: nitrogen; O: oxygen

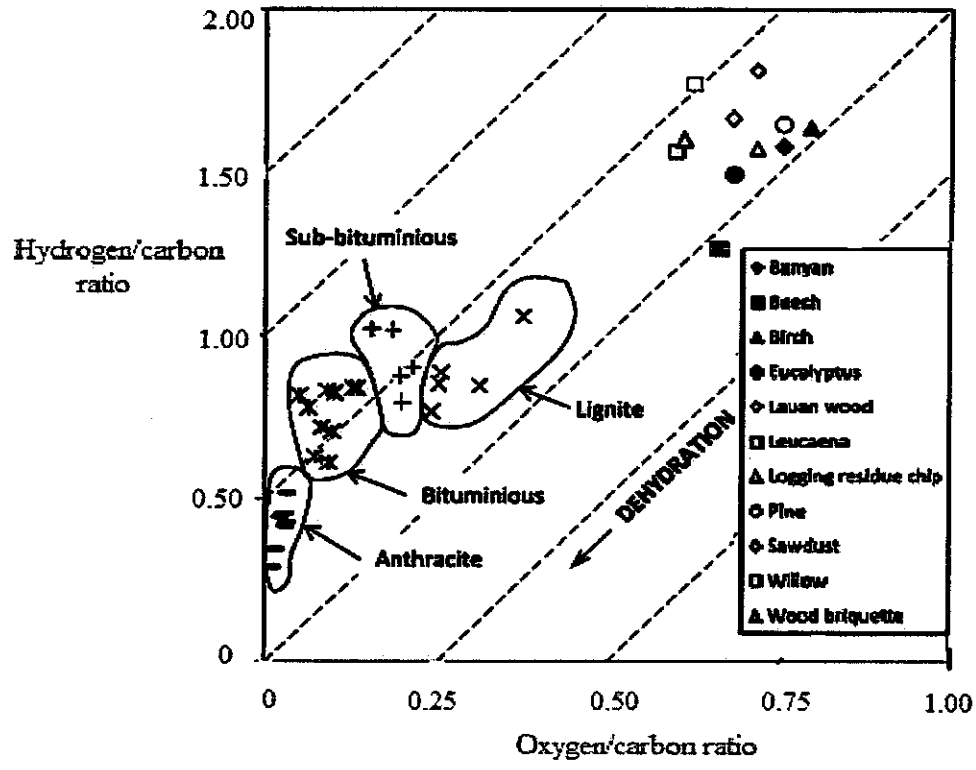


Figure 2.15 Coal sample and untreated biomass (Chew and Doshi, 2011).

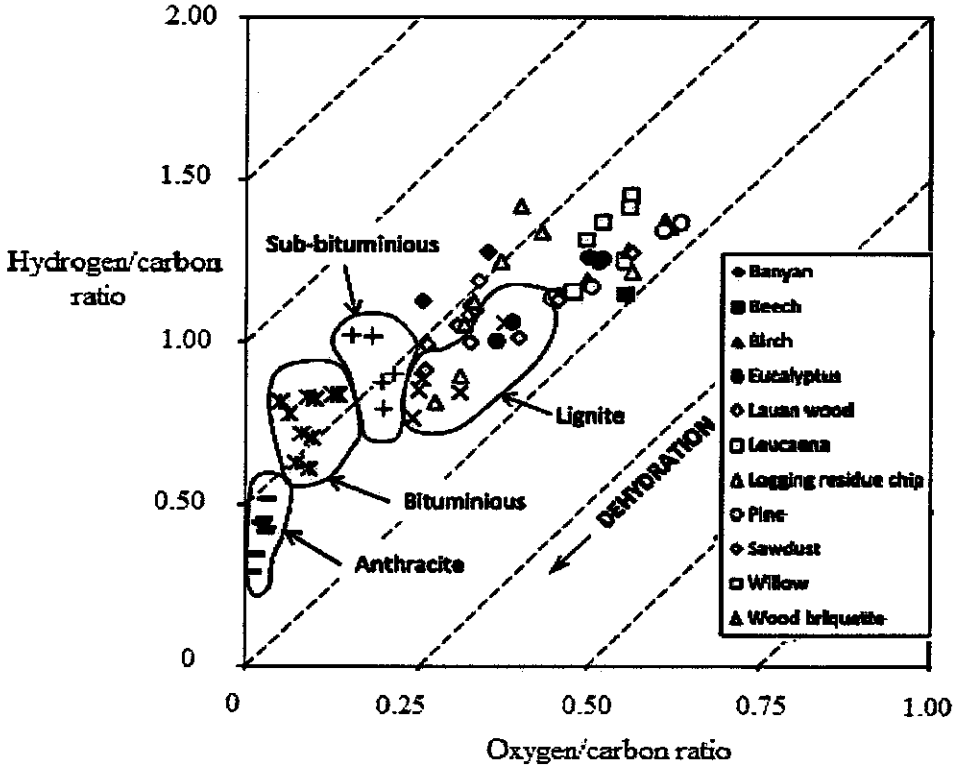


Figure 2.16 Coal sample and torrefied biomass above than 250 °C (Chew and Doshi, 2011).

Mayoral et. al. (2001) had also described the general stages involved during proximate analysis by using thermogram of thermal gravimetric analysis (TGA) as presented in Figure 2.17. In general, the proximate analysis was performed under nitrogen atmosphere. They have reported that the determination of moisture loss and volatile matters were determined in the nitrogen atmosphere. The moisture content was determined at the temperature ranges of 100 to 105 °C. Meanwhile, at the temperature ranges of 300 to 600 °C, volatile matters had measured due to biomass devolatilization occurred. The solid residue remained after devolatilization was called as char (fixed carbon). The char was further combusted at temperature around of 700 to 800 °C in the air atmosphere in order to determine the ash content.

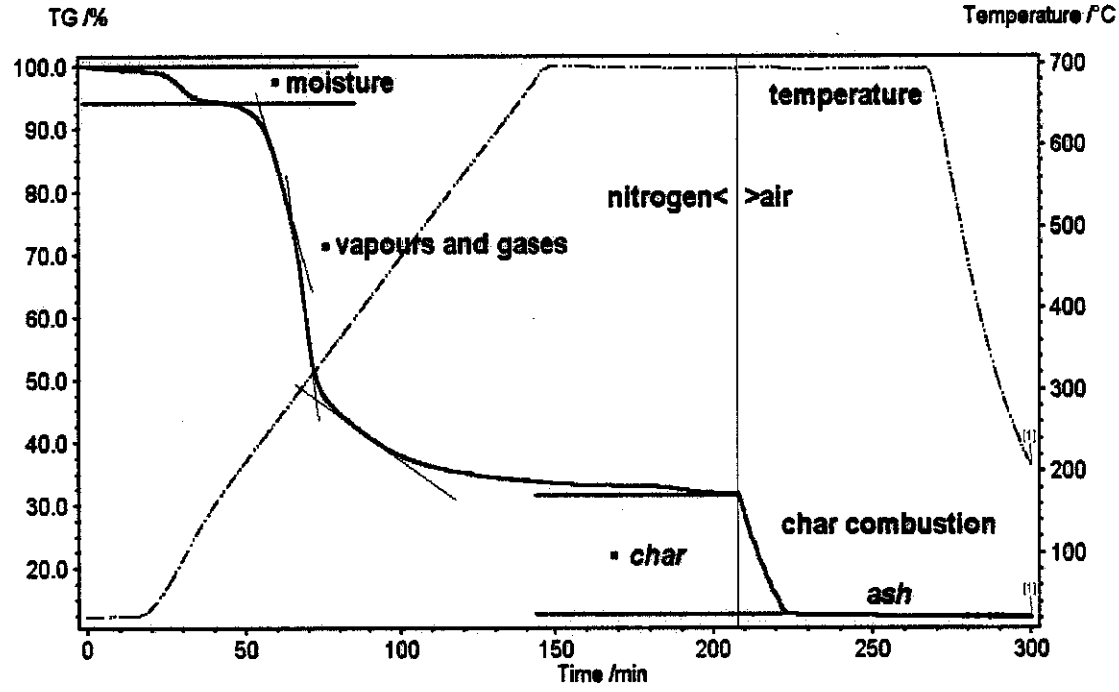


Figure 2.17 General stages of proximate analysis (Mayoral et. al., 2001).

2.7.2 Mass and Energy Yields

In biomass energy applications, torrefaction process is used to improve properties of the original biomass to make them suitable as fuel. However, this should be achieved without losing too much chemical energy to volatile matter loss during the process. Hence, the mass and energy yields were considered to be crucial parameters to evaluate the torrefaction process. Mass and energy yields of various torrefied biomass for torrefaction of 0.5 h and 1.0 h are tabulated in Table 2.5.

Table 2.5 Mass and energy yields and high heating value (HHV) of torrefied biomass for torrefaction of 0.5 h and 1.0 h (Chew and Doshi, 2011).

Biomass	t (h)	T (°C)	MY (wt.%)	EY (wt.%)	HHV (MJ/kg)
Woody biomass					
Logging residue chip	0.5	225	88.00	97.93	19.79
	0.5	250	81.00	92.68	21.21
	0.5	275	70.00	91.48	22.03
Leucena	0.5	200	91.00	94.14	21.00
	0.5	225	86.50	90.33	21.20
	0.5	250	73.00	76.24	21.20
	0.5	275	54.50	61.21	22.80
Pine	1.0	230	92.40	96.51	18.07
	1.0	250	88.20	94.37	18.51
	1.0	280	78.10	93.90	20.80
Willow	0.5	230	95.10	92.29	20.20
	0.5	250	89.60	85.39	21.40
	0.5	270	79.80	78.84	21.90
Non-woody biomass					
Baggase (sugarcane)	1.0	230	87.50	96.42	17.08
	1.0	250	78.90	92.03	18.08
	1.0	280	68.60	82.90	18.73
Mesocarp	1.0	220	63.08	61.21	19.03
(oil palm)	1.0	250	60.04	58.91	19.24
	1.0	300	52.45	59.30	22.17
Empty fruit bunches	1.0	220	43.16	43.54	43.54
(oil palm)	1.0	250	36.98	38.39	38.39
	1.0	300	24.18	29.00	29.00
Kernel shell	1.0	220	77.44	73.80	18.85
(oil palm)	1.0	250	73.83	71.18	19.07
	1.0	300	71.27	78.12	21.68
Reed canary grass	0.5	250	83.00	85.13	20.00
	0.5	270	72.00	76.80	20.80
	0.5	290	61.50	68.75	21.80

* t: time; T: temperature; MY: mass yield; EY: energy yield; HHV: higher heating value

The mass yield of torrefied biomass can vary from 24% to 95% of its original weight. In comparison, conversion rate of mass yield for non-woody biomass (agricultural residues) is higher than woody biomass. This is due to higher hemicelluloses content in the agricultural residues, thus contributing in lower mass yield (Uemura et. al., 2011; Deng et. al., 2009; Bridgeman et. al., 2008). Chew and Doshi (2011) also stated that energy yield which is calculated based on the mass yield and calorific value can be used as an indicator of the amount of energy loss during torrefaction. For all biomass, the energy yield was found to be greater than mass yield, and the effect became more significant for higher temperature of torrefaction process.

The energy yield for the woody biomass when subjected to torrefaction temperature below 250 °C was above 95% except for Lucerne wood which was only 88%. As torrefaction temperature increased to above 250 °C, the energy yield varied from 55% to 98%. Meanwhile, the non-woody biomass have wider ranges of energy yield as compared with the woody biomass, which were ranging from 29% to 98%. This was due to higher variation in volatile matters and hemicelluloses fraction of this biomass (Deng et. al., 2009). Moreover, they have found that the effect of torrefaction duration was less significant as compared with torrefaction temperature. They have suggested that the ideal torrefaction process condition was at moderate torrefaction temperature, in the range of temperature between 225 to 275 °C coupled with shorter torrefaction duration, which was less than one hour to minimize the energy loss in the torrefied biomass (Chew and Doshi, 2011).

According to Chew and Doshi (2011), the mass loss was dominated by the dehydration and devolatilization of hemicellulose fraction. Their findings supported by the observation on the mass spectrometry analysis. This analysis proved that the weight loss was initially resulted from the reduction in the moisture and followed by the decomposition of hemicellulose and primary lignin fraction. The studies have also reported that the composition of hemicellulose, cellulose and lignin of the feedstock affected the reactivity of torrefaction process (Chen and Kuo, 2010a; Almeida et. al., 2010; Prins et. al., 2006a). The hemicellulose was the most reactive under torrefaction condition followed by cellulose and lignin.

Furthermore, it can be concluded that increasing torrefaction temperature and residence time, have improved higher heating value (HHV) of biomass as shown in Table 2.6. After torrefaction process, the calorific values of woody and non-woody biomass have increased to the range of 18-26 MJ/kg and 17-23 MJ/kg, respectively. The calorific value increments of this torrefied biomass were 12-23% as compared with the raw biomass.

2.7.3 Mass Loss as the Indicator of Torrefaction Severity

According to Almeida et. al. (2010), their studies had proposed that the mass loss was an excellent indicator for the severity of torrefaction conditions. They have conducted studies on torrefaction of eucalyptus wood for two different species which were *E. grandis* and *E. saligna*, at two different residence times of 1 and 5 hours, at three temperatures levels of 220, 250 and 280 °C. They have selected fixed carbon and gross calorific value as the trial parameters. In order to study the relationship between these parameters with mass loss, they have made a graph of mass loss as function of fixed carbon as presented in Figure 2.18 and a graph of mass loss as function of gross calorific value as presented in Figure 2.19.

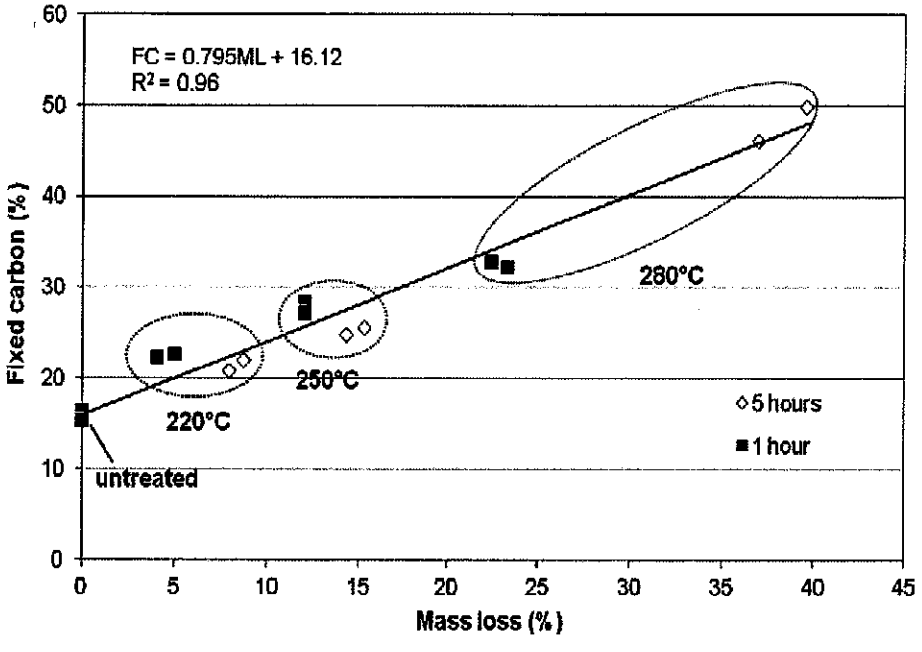


Figure 2.18 Fixed carbon as function of mass loss of *E. grandis* and *E. saligna* wood treated for 1 and 5 hours at three different torrefaction temperatures.

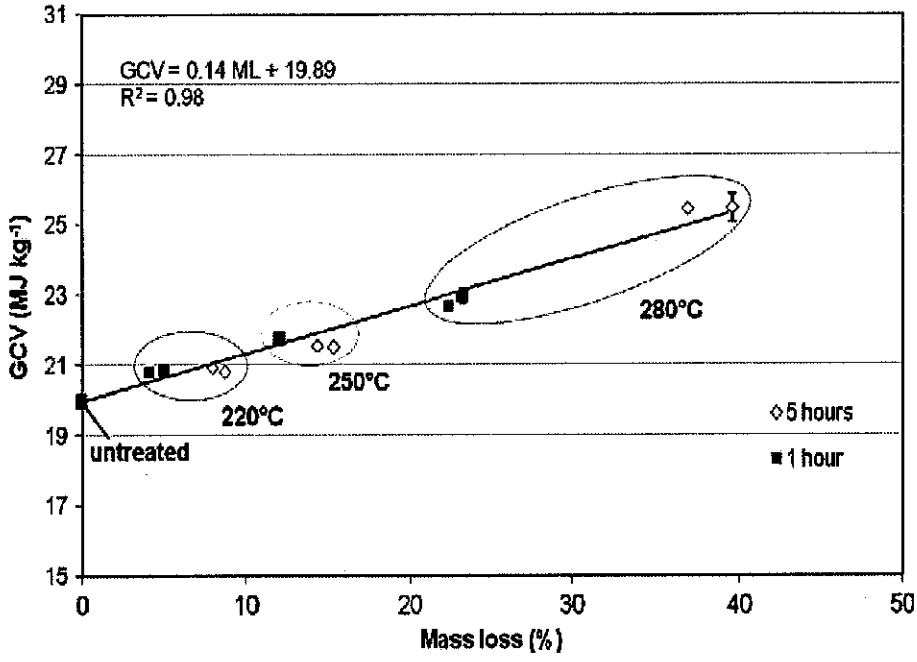


Figure 2.19 Gross calorific value as function of mass loss of *E. grandis* and *E. saligna* wood treated for 1 and 5 hours at three different torrefaction temperatures.

From the studies, they have reported that there were good correlations between the carbon content and gross calorific value with the mass loss. In addition, linear relationship was found between these two species with $R^2 = 0.96$ for mass loss as function of fixed carbon and $R^2 = 0.98$ for mass loss as function of gross calorific value. Therefore, their studies concluded that mass loss was a useful synthetic parameter for determining the effect of torrefaction conditions such as temperature and residence time on the biomass properties. Besides, the gross calorific value and carbon content were also crucial parameters that need to be considered in order to study the relationship between the mass loss and torrefaction severity.

2.7.4 Microscopic Observation of the Internal Structure

In order to observe the impact of the torrefaction on the internal structure of the torrefied biomass, scanning electron microscope (SEM) was employed. For instance, Figure 2.20 shows the SEM images of raw and torrefied *Lauan* wood as reported by Chen et. al. (2011a) while Figure 2.21 shows the SEM images for raw and torrefied bamboo as reported by Chen et. al. (2011b).

They have found that increasing the severity of torrefaction temperature could enhance the impact of decomposition on the internal structure (Chen et. al., 2011a, Chen et. al., 2010b). For example, the internal structure of *Lauan* wood that have been torrefied at the temperatures of 220 and 250 °C, the wood were characterized as the cell structures. Meanwhile, at the temperature of 280 °C, the surface structure was further damaged and clearly exhibited as tubular-shape. Chen et. al. (2011b) had also reported that the impact of torrefaction on the internal structure of biomass can be clearly observed in the SEM images. At the torrefaction temperature of 290 °C, the particle surface of bamboo was filled with tiny holes. These observations have also been found by the studies that conducted by Arias et. al. (2008).

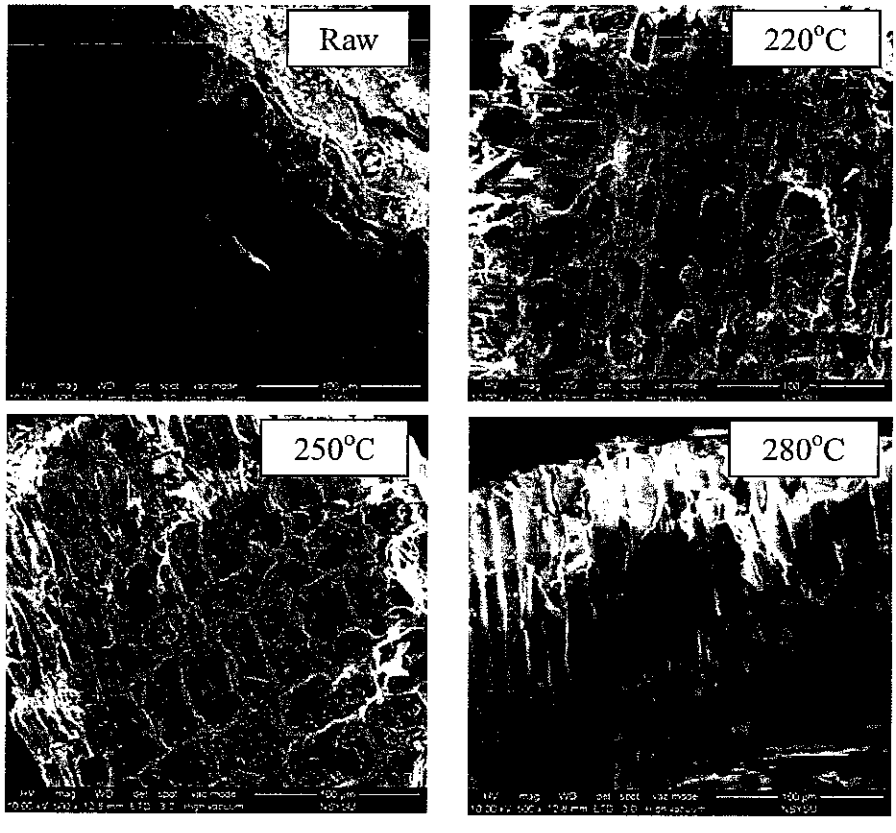


Figure 2.20 SEM images of raw and torrefied *Lauan* wood at three different torrefaction temperatures (Chen et. al., 2011a).

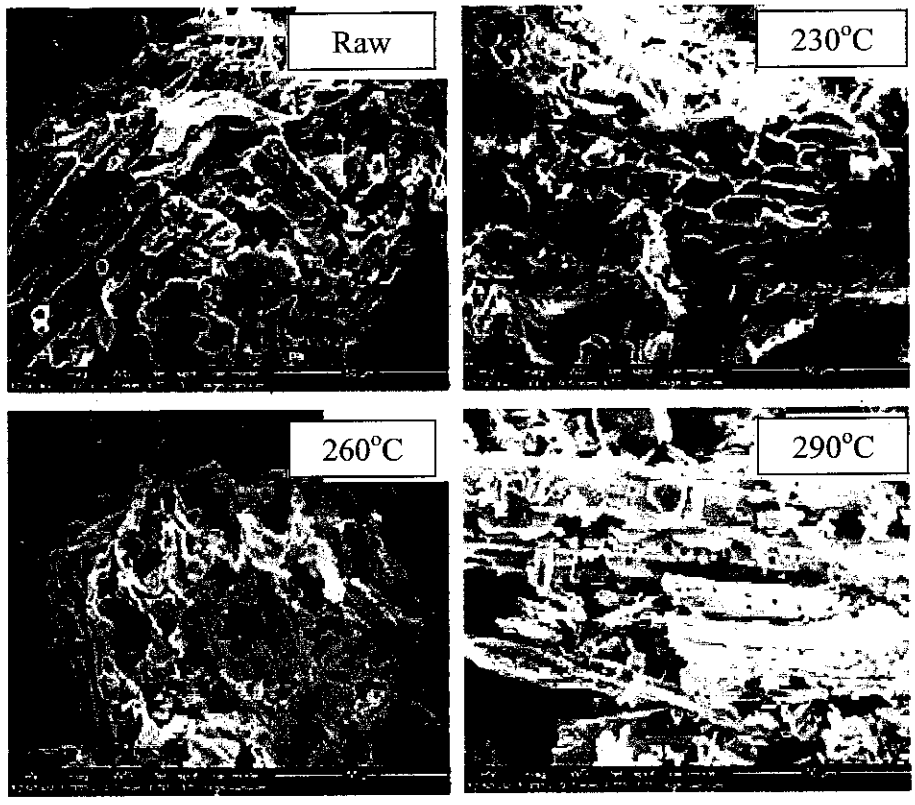


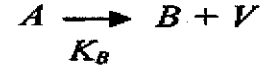
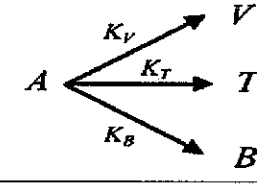
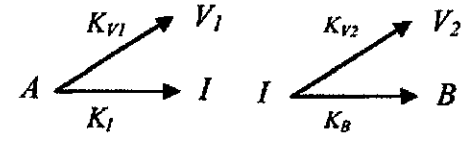
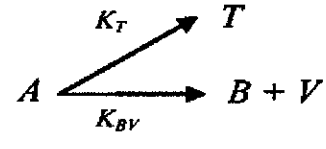
Figure 2.21 SEM images for raw and torrefied bamboo at three different torrefaction temperatures (Chen et. al., 2011b).

2.8 Mathematical Models for Torrefaction Kinetic

Generally, the reaction kinetics studies on the rate of chemical reaction as well as the factors affect the rate of reaction. In order to choose appropriate operation condition and for design of equipment, fundamental understanding of the reaction mechanism and kinetics are important. The mathematical models for torrefaction kinetic were mainly derived from the biomass pyrolysis (Chew and Doshi, 2011; Repellin et. al., 2010; Prins et. al., 2006b). Biomass composed of mainly hemicelluloses, cellulose and lignin. Each of them had different thermal stability which influenced the characteristic of biomass pyrolysis. Chew and Doshi (2011) have reported that the biomass pyrolysis can be classified into four main regions. At the low temperature less than 220 °C, the moisture evolution was the main reaction mechanism. Then, hemicellulose degradation had followed at temperature above than 200 °C while the cellulose decomposition continued from 200 to 400 °C. In contrast, the lignin had started slowly decomposed from 160 until 900 °C.

Due to the torrefaction temperature in the range of 200 to 300 °C, the main reaction included the moisture evolution, the hemicellulose fraction decomposition and limited decomposition of lignin and cellulose fractions (Arias et al., 2008; Prins et. al., 2006a). Hemicellulose decomposition can be well described by a two-step mechanism as found by Di Blasi and Lanzetta (1997). The first reaction was took place at the temperature below 250 °C, where the depolymerisation had rearranged the polysugar structures. Then, it proceeds with the decomposition of the oligosaccharides and monosaccharides at the higher temperatures of 250 to 300 °C, which resulted in the formation of char, CO, CO_2 and water.

Table 2.7 Kinetic models that have been applied for torrefaction studies.

Biomass	Temperature (°C)	Kinetic model
Spruce and beech (Repellin et. al., 2010)	220-260	One step global model 
Wood, wood log and briquettes (Chew and Doshi, 2011)	130-280	Three parallel reactions model (Shafizadeh and Chin model) 
Willow (Bergman et. al., 2005a; Prins et. al., 2006b) Spruce and beech (Repellin et. al., 2010)	220-300	Two step consecutive model (Di Blasi-Lanzetta model) 
Spruce and beech (Repellin et. al., 2010)	220-260	Two parallel reactions model (Broido-Shafizadeh model) 

where ***A*** is the biomass, ***B*** is the solid product, ***I*** is the intermediate compounds, ***T*** is the tar, and ***V*** is the volatiles.

In addition, Table 2.7 summarizes several kinetic models that have been applied for studies of torrefaction process. One step global model was the simplest for kinetic model, where the overall biomass thermal degradation was modelled as a single step with first order reaction. The one step global model was used for the anhydrous weight loss kinetic of torrefaction spruce and beech (Repellin et. al., 2010). Good fitting between the calculated and experimental anhydrous weight loss (R^2 of 0.961 to 0.993) was reported. They have assumed that the thermal decomposition of spruce and beech to be similar and the activation energy of 92.0 kJ/mol. The resulting kinetic constant had fitted the predicted reactivity of hardwood versus softwood. However in practical application, this single step model was not applicable for the prediction of product yield due to the assumption of fixed ratio of pyrolysis process products (Di Blasi and Lanzetta, 1997).

Furthermore, several studies have adopted a two step consecutive model which is the Di Blasi-Lanzetta model for the weight loss kinetics for woody biomass (Bergman et. al., 2005b; Repellin et. al., 2010; Di Blasi and Lanzetta, 1997). An intermediate reaction product was proposed for secondary devolatization reactions were introduced in this model. For the temperature ranges of 230 to 300 °C, the kinetics of torrefaction reactions had been described by two consecutive first order reactions, depicting the hemicellulose decomposition followed by the cellulose decomposition (Prins et. al., 2006b). The correlation using the Di Blasi-Lanzetta model was reported to fit better with R^2 value of 0.986-0.987 than the single step model for both hardwood and softwood (Repellin et. al., 2010). The good improvement fitting of this model had been attributed from the two step consecutive model that taken accounted the intermediate pseudo-components (Repellin et. al., 2010; Prins et. al., 2006b). Based on the kinetic parameters derived for the willow sample, the rate of the first reaction was higher than the second reaction (Chew and Doshi, 2011). Bergman et. al. (2005b) had suggested that it was due to the decomposition of cellulose and lignin which possibly catalyzed by the inorganic substance or the liquid and gases by-products.

Moreover, the thermal degradation of the lignocellulosic biomass was proposed to be three independent overlapping reactions of hemicellulose, cellulose and lignin. The model was studied in the torrefaction of beech and spruce (Repellin et. al., 2010). The hemicellulose breaks down first as also mentioned in the Di Blasi-Lanzetta model. Meanwhile, the lignin decomposition had adopted the single step model. Cellulose decomposition had suggested by the modified Broido-Shafizadeh model which represented by the two parallel reactions. They have obtained a good correlation between the model and experimental data. However, the predicted reactivity for beech and spruce contradicted with the experimental observation. As the lignocellulosic constituents of biomass samples were not totally independent in decomposition, the decomposition of the hemicelluloses and cellulose was proposed to be modelled with the introduction of pseudo-components to deal possible interaction between the constituents.

According to Chew and Doshi (2011), for torrefaction of larger biomass particle such as wood log and briquettes, Shafizadeh and Chin model have been adopted. The model consisted of three parallel pathways of the pyrolysis for wood which to be degraded into char, tar and volatile. The model and experimental data fitted relatively well for temperature ranges between 230 to 260 °C. However, beyond temperature of 260 °C, the model failed to fit the experimental data. They have suggested that it was possibly due to the initiation of carbonization reaction which was not accounted in the model. Besides, a studies on the temperature integral approximation that proposed by Agrawal and Sivasubramanian (1987) is adopted to estimate the reactivity of thermally treated biomass under the non-isothermal decomposition (Arias et al., 2008). The combustibility curve of the torrefied samples was represented by two stages. In general, the derived kinetic parameters had indicated that the activation energy of the first stage varies with the residence time while the second stage remained relatively constant.

2.9 Chapter Summary

In this chapter, the theoretical backgrounds of biomass energy and torrefaction process are highlighted. The fundamental of torrefaction process, properties of torrefied biomass and its characterization is presented to enable better understanding about this topic. The effects of torrefaction temperature and torrefaction time on the elemental composition, calorific value, mass and energy yields of torrefied biomass have been discussed. The influences of composition and decomposition temperature of hemicellulose, cellulose and lignin of oil palm biomass on the properties of torrefied biomass are also discussed as well. In addition, several studies on the modeling work that have been done for torrefaction kinetic are also presented.

CHAPTER THREE

EXPERIMENTAL

3.1 Chapter Overview

This chapter describes the overall procedures in this research work. In section 3.2, sample preparation is described include the collection of biomass, drying, grinding and sieving. The description of experimental set up such as the details procedures for torrefaction process in the TGA and tube furnace are presented in section 3.3. In section 3.4, it describes the entire characterization of the biomass such as the calorific value, proximate, ultimate and lignocellulosic analyses as well as microscopic observation by SEM. The calculations of kinetic parameters and absolute average deviation (AAD) are also included in this section.

3.2 Sample Preparation

Three types of oil palm biomass were selected which were empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS). They were randomly collected at the palm oil mill of FELCRA Nasharuddin at Bota, Perak in Malaysia. The materials were chopped into smaller size for easier handling. Then, they were dried in an oven model LHT 4/120 manufactured by Carbolite at 105°C for 24 hours to provide a basis of the tested materials. After drying, they were subjected to grinding process by using grinder manufactured by Fritsch. The grinded materials were submitted to sieving process by using siever size of 100-750 μm manufactured by CISA. They were sieved into particle size ranges of 250-355 μm and 355-500 μm. Then, the prepared biomass were transferred into labelled sample bottle and stored in the controlled cupboard that maintained at the room temperature.

3.3 Experimental Set-up

3.3.1 Torrefaction Process by TGA

Torrefaction process was carried out in the thermogravimetric analyzer (EXSTAR TG/DTA 6300-SII Japan). The functions of the TGA were to measure and record the dynamic of biomass weight loss with increasing temperature or time. For every run, approximately 2 mg of biomass was used. The tested sample was loaded in a ceramic pan, weighed and placed inside the TGA furnace. In this study, the heating rate was fixed at 10 °C min^{-1} along the process. Nitrogen gas was used as the carrier gas with the flow rate was fixed at 100 ml min^{-1}, therefore biomass was torrefied under an inert environment. Torrefaction temperatures were varied into six different temperatures namely 200, 220 and 240 °C which considered as mild torrefaction process while 260, 280 and 300 °C which considered as severe torrefaction process. During torrefaction process, the temperature programmes were based on the method that was proposed by Chen and Kuo (2010a) and Prins et. al. (2006b) with minor modifications in order to adapt to the TGA system.

The temperature programmes consisted of a dynamic heating period and an isothermal heating period. Specifically, the TGA temperature was raised from 50 to 120 °C and maintained for 10 minutes to remove moisture in the biomass. Then, the temperature was raised from 120 °C to six different final torrefaction temperatures namely 200, 220, 240, 260, 280 and 300 °C. Once the temperature of TGA was reached to the final torrefaction temperature, the biomass was torrefied for 120 minutes. For example, to perform torrefaction process at 260 °C, biomass was heated from 50 to 120°C and maintained for 10 minutes. Then, biomass was further heated by raising temperature from 120 to 260 °C, and the biomass was torrefied for 120 minutes. Preliminary studies have been carried out to determine an appropriate torrefaction time for oil palm biomass such as 60, 90 and 120 minutes. From the work, torrefaction time of 120 minutes was selected for a complete decomposition reaction of EFB, PMF and PKS. Finally, after the torrefaction process was completed, the TGA furnace automatically cools down to 50 °C to provide a stable temperature and to prepare for the next runs.

3.3.2 Torrefaction Process by Tube Furnace

Due to a lesser amount of the torrefied biomass (in mg) that had been produced in the TGA, tube furnace was used to produce significant amount of torrefied biomass for further analyses. The produced torrefied biomass in the tube furnace was used to conduct the ultimate analysis, microscopic observation and calorific value determination. In this work, tube furnace model TSH17/75/450-2416-2116 which manufactured by Elite Thermal Systems Limited was used. All the same temperature programmes in the TGA were repeated again in the tube furnace. Firstly, the tube furnace was switched on as well as the nitrogen gas tank. After that, the valve was opened to allow the nitrogen gas flowing into tube furnace.

Approximately, 2 g of biomass was inserted into a ceramic pan (ship shape) and placed into the tube furnace. During the torrefaction process, the nitrogen gas flow was fixed at 100 ml min^{-1} while the heating rate was fixed at 10 °C min^{-1}. The parameters such as the heating rate, final torrefaction temperature, reaction time and ending conditions were controlled on the display screen of the tube furnace. After all the required parameters have been set, the isolated button was pressed followed by the run button that located on the display screen of the tube furnace. After the process was completed, the temperature of tube furnace was reduced to 50 °C in order to provide stable temperature for the next runs.

3.4 Characterization

3.4.1 Proximate Analysis

Proximate analysis was carried out to determine moisture, ash and volatile matter content for raw biomass. The analysis was done based on two methods; the first method was done by using a Carbolite furnace as described by ASTM-D5142-04 and the second method was the thermal gravimetric method which was done by using thermogravimetric analyzer (TGA) as proposed by Mayoral et. al. (2001) and Heikkinen et. al. (2004) with minor modification.

(a) Proximate analysis in the Carbolite furnace accordance to ASTM D5142-04

(i) Moisture content

A ceramic crucible was weighed, W_c and approximately, 1.0 g of dried biomass was placed into the weighed crucible, W_i. Then, it was submitted in the furnace at temperature of 105 °C for 1 hour drying. After completed, the crucible was taken out and cooled in desiccator at room temperature. The crucible was weighed after cooling and recorded as W_f. It was weighed again until the successive mass loss was less than 2 mg. The moisture content was calculated as follows:

$$\text{Moisture content (\%)} = \frac{W_i - W_f}{W_i - W_c} \times 100 \qquad (3.1)$$

where;

W_c = crucible weight, in grams

W_i = initial weight crucible, in grams

W_f = final weight crucible, in grams

(ii) Ash content

A known weight of empty crucible was recorded as W_c. Then, approximately 1.0 g of biomass was inserted into the crucible and weighed, W_i. The crucible filled with biomass was submitted into the furnace. The furnace was heated from room temperature to 500 °C and maintained for 1 hour. Then, it was continued heating until 700 °C and maintained for 2 hours. After completed, the crucible with ash residues was left to cool in dessicator and weighed, W_f. The ash content was calculated from the formula as follows:

$$\text{Ash content (\%)} = \frac{W_i - W_f}{W_i - W_c} \times 100 \qquad (3.2)$$

where;

W_c = crucible weight, in grams

W_i = initial weight crucible, in grams

W_f = final weight crucible, in grams

(iii) Volatile matter content

A crucible with cover was weighed and recorded as W_c. Approximately, 1.0 g of biomass was placed into the weighed crucible with cover and record as initial weight, W_i. The crucible was then closed tightly with its cover, so that no carbon deposit was burnt from the underside. Next, it was placed into the furnace and heated at temperature of 950 °C, and maintained for 7 minutes. After completed, the crucible was cooled in dessicator without replacing its cover and weighed, W_f. The percentage of volatile matter was determined as follows:

$$\text{Weight loss (\%)}, A = \frac{W_i - W_f}{W_i - W_c} \times 100 \qquad (3.3)$$

Volatile matter (%) = weight loss %, A – moisture %, as determined in (i)

where;

W_c = crucible weight with cover, in grams

W_i = initial weight crucible with cover, in grams

W_f = final weight crucible with cover, in grams

(iv) Fixed carbon content

The percentage of fixed carbon content was determined as follows:

Fixed carbon content (%) = 100 – (moisture + volatile matter + ash content) (3.4)

(b) Proximate analysis accordance to thermal gravimetric method

The analysis was carried out by using a thermogravimetric analyzer (EXSTAR TG/DTA 6300-SII Japan) together with TG controller. The weight changes as the function of temperature or time were monitored. TGA consisted of a sample pan that suspended from the weighing mechanism with wire.

The furnace can withstand up to 1100 °C and the reactor temperature was measured by a chromel-alumel thermocouple that exactly located below the sample pan. Pure, dry nitrogen gas was passed through the balance housing and furnace. The gas tank low-pressure regulator was set up to allow smooth environment of switch-over gas process. Hence, the measurement of the balance was not disturbed during switching the gas. The microprocessor was automatically switched the gas inlet valve from nitrogen and oxygen at the appropriate time to initiate combustion (Mayoral et. al., 2001; Elder, 1983). In general, about 5-10 mg biomass was placed in the tarred sample pan and placed in the furnace. The temperature was raised according to the temperature programming. The weight percent was set up as 100% on the recorder chart and the dynamic of weight was recorded along the process. This unit controlled all the automatic function of the recorder and temperature programming of the furnace (Elder, 1983).

In the present work, the procedure was carried out based on the method that proposed by Heikkinen et. al. (2004) and Mayoral et. al. (2001) with minor modification in order to adapt with the system of TGA. Approximately, 5 mg of biomass at the size of 250-355μm was placed in the tarred sample pan. The nitrogen gas flow rate was fixed at 100 ml min^{-1} along the process. At first, the system was maintained at 30 °C for 5 minutes to allow the biomass to loose any adsorbed moisture and also to let the furnace purged out the air. Then, biomass was heated from 50 to 110°C at the constant heating rate of 60 °C min^{-1}. It was maintained isothermally for 5 minutes to determine moisture content in the biomass. After that, it was further heated with constant heating rate of 100 °C min^{-1} until reached 900 °C. It was maintained only for 5 minutes to determine the percentage of volatile matter in the biomass. Although ASTM standard has proposed that in order to determine ash content by combustion at 750 °C, but researchers have found that it was unnecessary to cool down the system from to this temperature before initiating the combustion. Thus, in the present study, for determining the ash content, the purge gas was automatically switched to oxygen (99.9%) with flow rate of 30 ml min^{-1}. The fixed carbon in the biomass was burn-off and oxidized, leaving the residues that accounted as the ash content.

3.4.2 Lignocellulosic Analysis

The lignocellulosic analysis was carried out to determine the hemicellulose, cellulose and lignin content in the feedstock. It was performed according to the adaptation method from Wood Industry Handbook (1982). The analysis consists of three main parts and is discussed as follows:

(i) Determination of holocellulose content

Holocellulose is the sum of hemicellulose and cellulose content in the biomass. Firstly, 3 g of biomass was treated in 120 ml of 0.3% chlorine water. The solution was allowed to stand about 5 minutes for the chlorination process. Then, the solution was filtered by using vacuum filtration with washing of 250 ml of 5% sulphurous acid aqueous solution and 500 ml of distilled water. The second step was transferred the filter cake produced from filtration into 100 ml beaker and 50 ml of 2% sodium sulphite solution was added. Then, the beaker was left in the boiling water bath for 30 minutes. Again, after 30 minutes the solution was filtered. The first and second steps were repeated for three times until the colour of filter cake became lighter than the colour of raw biomass. Thirdly, the filter cake was transferred into 100 ml beaker and 20 ml of 0.1% potassium permanganate aqueous solution was added. The beaker was left for about 10 minutes. Next, small amount of 3% sulphurous acid aqueous solution was added to neutralize the solution.

Fourthly, the solution was transferred into 200 ml beaker that filled with 200 ml of distilled water. The beaker was placed in boiling water bath for 1 hour. Again, the solution was filtered with washing of 500 ml of hot distilled water and then small amount of 95% ethanol was added. Finally, the filter cake was dried at 105 °C (plus minus 3 °C) for 4 hours. The residue was cooled down naturally in desiccator for 30 minutes and weighed. After that, the residue was dried again at 105 °C (plus minus 3 °C) for 1 hour, cooled down in the desiccator for 30 minutes and weighed. The drying process was repeated until the weight difference become less than 2 mg. The hemicellulose content was calculated as the difference between the holocellulose and α-cellulose content (second part).

(ii) Determination of α-cellulose content

The residue from the determination of holocellulose (first part) was used in this step. Approximately 2.0 - 2.5 g of residue was placed into 200 ml conical flask and 120 ml of 17.5 wt% sodium hydroxide aqueous solution was added. The solution was stirred by a magnetic stirrer at ambient temperature for 24 hours. After the process completed, the solution was filtered by using the vacuum filtration with distilled water. Finally, the filter cake was dried at 105 °C (plus minus 3 °C) for 4 hours. The residue was cooled down naturally in desiccator for 30 minutes and weighed. After that, the residue was dried again at 105 °C (plus minus 3 °C) for 1 hour, cooled down in desiccator for 30 minutes and weighed. The drying process was repeated until the weight difference become less than 2 mg. The residue from the determination of α-cellulose content was considered as the cellulose content.

(iii) Determination of lignin content

Firstly, 1 g of biomass was placed into 100 ml of beaker and 15 ml of 75% sulphuric acid. The solution was left at the 20 °C water bath for 4 hours. Then, the solution was transferred into 1 litre conical flask with filled of 560 ml of distilled water. The solution was refluxed for 4 hours in the boiling water bath. After that, the solution was filtered by using the vacuum filtration with washing 500 ml of distilled water. Finally, the filter cake was dried at 105 °C (plus minus 3 °C) for 4 hours. The residue was cooled down naturally in desiccator for 30 minutes and weighed. After that, the residue was dried again at 105 °C (plus minus 3 °C) for 1 hour, cooled down in the desiccator for 30 minutes and weighed. The drying process was repeated until the weight difference become less than 2 mg. The residue remained was considered as the lignin content.

3.4.3 Ultimate Analysis

The ultimate analysis was carried out to measure the elemental composition of biomass in term of carbon, hydrogen, nitrogen and sulphur content for raw and torrefied biomass. The analysis was conducted accordance to standard practice by ASTM-D3176-89. It was performed by CHNS analyzer model CHN-900/CHNS-932 manufactured by LECO. Approximately, 2 mg of biomass was placed into the CHNS tin capsule. Then, the tin capsule was wrapped properly and weighed. The wrapped samples were placed into the slot inside the analyzer and the process was started. After the analysis completed, the values for each elements were recorded. For each biomass, it was repeated in triplicate and to get the average values.

3.4.4 Gross Calorific Value (GCV) Determination

The gross calorific value (GCV) for each raw and torrefied biomass was measured by using bomb calorimeter model C2000 series manufactured by IKA-WERKE. The measurements of GCV were conducted accordance to ASTM D5865-03. The GCV was determined as the basis of thermal energy that generated from the complete combustion of biomass under constant pressure in the chamber. Firstly, the bomb calorimeter, oxygen tank regulator and cooling fan was turned on and waited about 15 minutes to provide stable environment. Approximately, 0.5 g of biomass was weighed and placed into the crucible. A cotton thread was tied up at the ignition wire and the crucible was placed inside decomposition vessel. On the main screen of bomb calorimeter, the biomass weight was recorded. After that, the start button was pressed and the system was running. Finally, the obtained GCV of the torrefied biomass was further used to calculate energy yield.

3.4.5 Microscopic Observation

In order to gain deeper insight on the impact of torrefaction on the internal structure of the torrefied biomass, the scanning electron microscope (SEM) model 1430 made in Germany was employed. For the conventional technique of SEM, the samples need to be electrically conductive at least at the surface, and electrically

grounded to prevent the accumulation of electrostatic charge at the surface. Therefore, they are usually coated with an ultra thin coating of electrically-conducting materials. Currently, conductive materials used for sample coating included gold, gold/palladium alloy, platinum, chromium and graphite. The process of deposition of conductive materials onto the samples can be done either by low vacuum sputter coater or high vacuum evaporator. The coating process is necessary in order to increase the signal and surface resolution.

In the present work, each raw and torrefied EFB, PMF and PKS at particle size of 355-500 μm were submitted into SEM. To compare the images of raw biomass with torrefied biomass, only three torrefaction temperatures were selected which biomass that have been torrefied at 220, 260 and 300 °C; respectively. Before the analysis, the sample preparation was conducted. Firstly, the biomass was stick onto the specimen holder called as specimen stub and submitted to coating process. During the coating process, the low vacuum sputter coater was used to coat the biomass with the gold/ palladium alloys. After biomass had been coated, it was submitted into the SEM where the images were recorded at 5000x magnification.

3.4.6 Kinetic Parameters Calculation in Modelling Work

The distribution weight loss from torrefaction process by using TGA was used in the modelling work. A model for torrefaction process was created through MATLAB in order to predict the amount of torrefied biomass produced from different feedstock namely EFB, PMF and PKS at the different torrefaction temperature. Before the modelling work, kinetic parameters calculation was carried out. In order to identify reaction order, n of torrefaction process, the graphical method was used which by plotting two types of graphs. The first graph is a graph of $\ln \frac{[W(t)]}{[W(0)]}$ versus time which to verify it is the first order reaction while a graph of $\frac{1}{[W(t)]} - \frac{1}{[W(0)]}$ versus time in order to verify it is the second order reaction. If the plotted graph straight line was obtained, the reaction order was valid for this process.

The slope of the graph represented the rate constant and it will used for determining of the activation energy, E_a and pre-exponential factor, A. Furthermore, the rate constant, k_1 or k_2 was obtained by plotting the graph of $\ln k$ versus $1/T$ which is derivation from Arrhenius equation as follows:

$$\mathbf{k1 \text{ or } k2} = Ae^{\frac{-Ea}{RT}}$$

$$\mathbf{\ln k1 \text{ or } \ln k2} = \left(\frac{-Ea}{R}\right)\frac{1}{T} + \mathbf{\ln A}$$

$$y = mx + c$$

Finally, absolute average deviation (AAD) was introduced to identify error between modelling and experimental data as follows:

$$\mathbf{AAD} = \frac{1}{n}\sum_{i=1}^{n}|xi|$$

where n is number of experiment or modelling data and x_i is error data.

3.5 Chapter Summary

In this chapter, the overall procedures that have been used are presented. It includes the description of sample preparation, an experimental set up with the details procedures of torrefaction process in the TGA and tube furnace. Besides, the entire procedures for characterizations of the biomass such as calorific value, proximate, ultimate and lignocellulosic analyses as well as the microscopic observation by SEM. The calculations of the kinetic parameters and AAD are also included.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Chapter Overview

This chapter presents the findings and outcomes of this work. Torrefaction of empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) between particle sizesof 250-500 μm have been carried out. The characterizations of raw materials such as calorific value, lignocellulosic, ultimate and proximate analyses are discussed in section 4.2. Meanwhile, the temperature profile of torrefaction process is presented in section 4.3. Furthermore, the characterizations and properties of torrefied biomass such as CHNS content, calorific value, weight loss distribution, mass loss, mass and energy yields and surface structure are highlighted in section 4.4. In addition, kinetic studies of torrefaction process is discussed in section 4.5 which includes the obtained kinetic parameters, a model that was developed by MATLAB and comparison between the modelling data with experimental data by using calculated AAD. Besides, the advantages or added values of torrefied oil palm biomass from these findings and its benefits for an industrial scale are discussed in section 4.6.

4.2 Characterization of Raw Materials

4.2.1 Lignocellulosic Analysis

The results of lignocellulosic analysis for raw EFB, PMF and PKS are summarized in Table 4.1. However, only particle size of 355-500 μm was selected to perform this analysis due to lack of the chemicals stock i.e sulphurous acid solution. In comparison with the present study, reported data by Mohammed et. al. (2011) is also listed in Table 4.1.

Table 4.1 Composition of raw EFB, PMF and PKS size 355-500 μm.

Components	Oil palm biomass size 355-500 μm (wt. %)					
	EFB*	EFB**	PMF*	PMF**	PKS*	PKS**
Hemicellulose	24.46	36.89	23.03	34.57	18.24	24.10
Cellulose	49.06	40.02	44.04	37.50	33.20	22.08
Lignin	26.48	23.09	32.94	27.93	48.56	53.82

* in the present study; ** from Mohammed et. al. (2011)

From the presented table, EFB contained the highest hemicellulose and cellulose content while PKS contained the highest lignin content. From these results, it was verified that each types of oil palm biomass have different composition of hemicellulose, cellulose and lignin that will affected their torrefaction process behaviour. The higher hemicellulose content will enhance the decomposition of EFB during torrefaction process while decomposition of PKS will predict to be less drastic during torrefaction process due to its high lignin content. In general, Mohammed et. al. (2011) had also reported that EFB contained the highest hemicellulose and cellulose followed by PMF and PKS. Meanwhile, PKS had the highest lignin content followed by PMF and EFB. However, when comparing the results from the present study with the reported data by Mohammed et. al. (2011), the composition of hemicellulose, cellulose and lignin were quite significantly different.

For instance, they have reported that EFB contained 36.89% of hemicellulose but the present study showed that EFB only contained 24.46% of hemicellulose. Besides, the present study revealed that PKS contained 33.20% of cellulose while Mohammed et. al. (2011) reported that PKS contained 22.08% of cellulose. However, for lignin content of EFB (26.48%) was quite comparable with reported data by Mohammed et. al. (2011) which was 23.09%. All these significant differences of the chemical composition of oil palm biomass between the present study and previous study might be related to the variation in their origins, species and location of the plantation area (Mohammed et. al., 2011).

In addition, the methods and procedures that have been used might be the factors that contributed to these differences. It was because the techniques applied, chemicals used and conditions during the experiment can affect the results. For example, in the present study, the analysis was done according to procedures in the Wood Industry Handbook (1982) while Mohammed et. al. (2011) had used the procedures in the Agricultural Handbook no. 379 by the USA Department of Agriculture. Nonetheless, both studies have showed similar trend of the composition of hemicellulose, cellulose and lignin content of these oil palm biomass.

4.2.2 Proximate Analysis

Proximate analysis was conducted by using two methods namely ASTM method (D5142-04) and thermal gravimetric method as proposed by Mayoral et. al. (2001) and Heikkinen et. al. (2004). All the thermograms of thermal gravimetric analysis for are presented in Figures 4.1 to 4.3. However, only particle size of 355-500 μm was selected to perform this analysis due to limited oxygen gas supply in the laboratory.

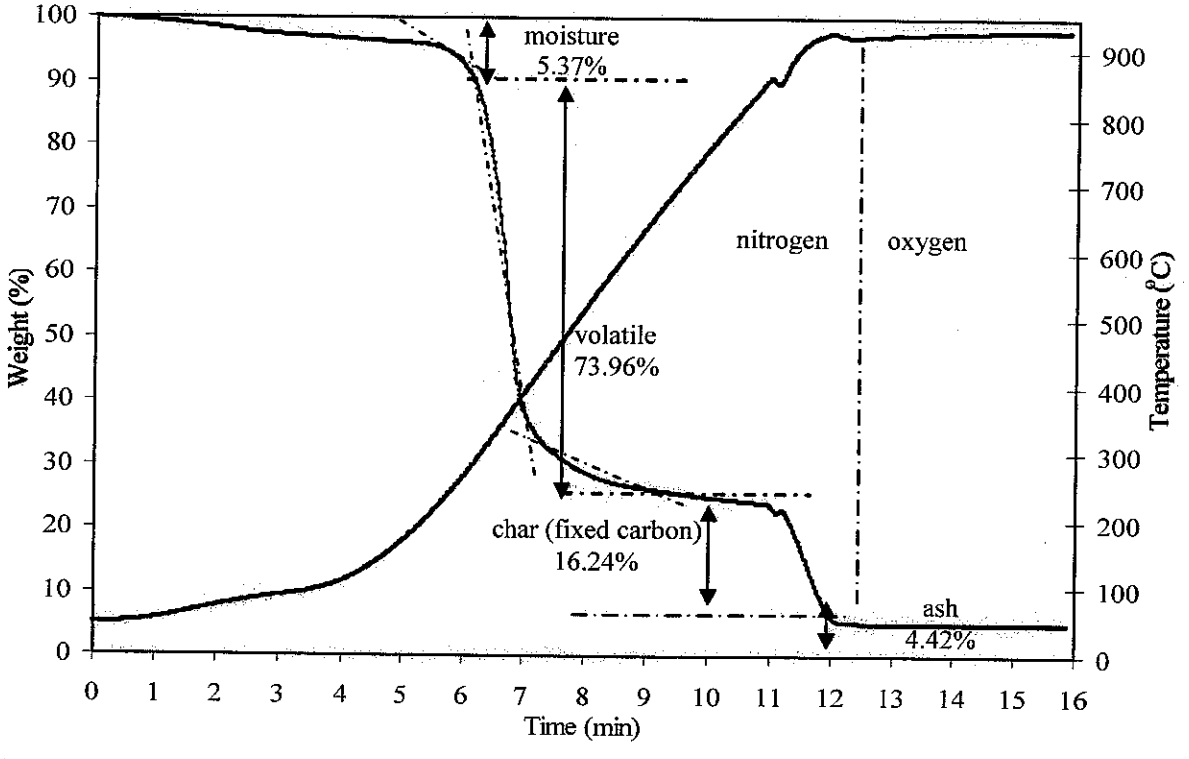


Figure 4.1 Thermogram of thermal gravimetric analysis for EFB size of 355-500 μm.

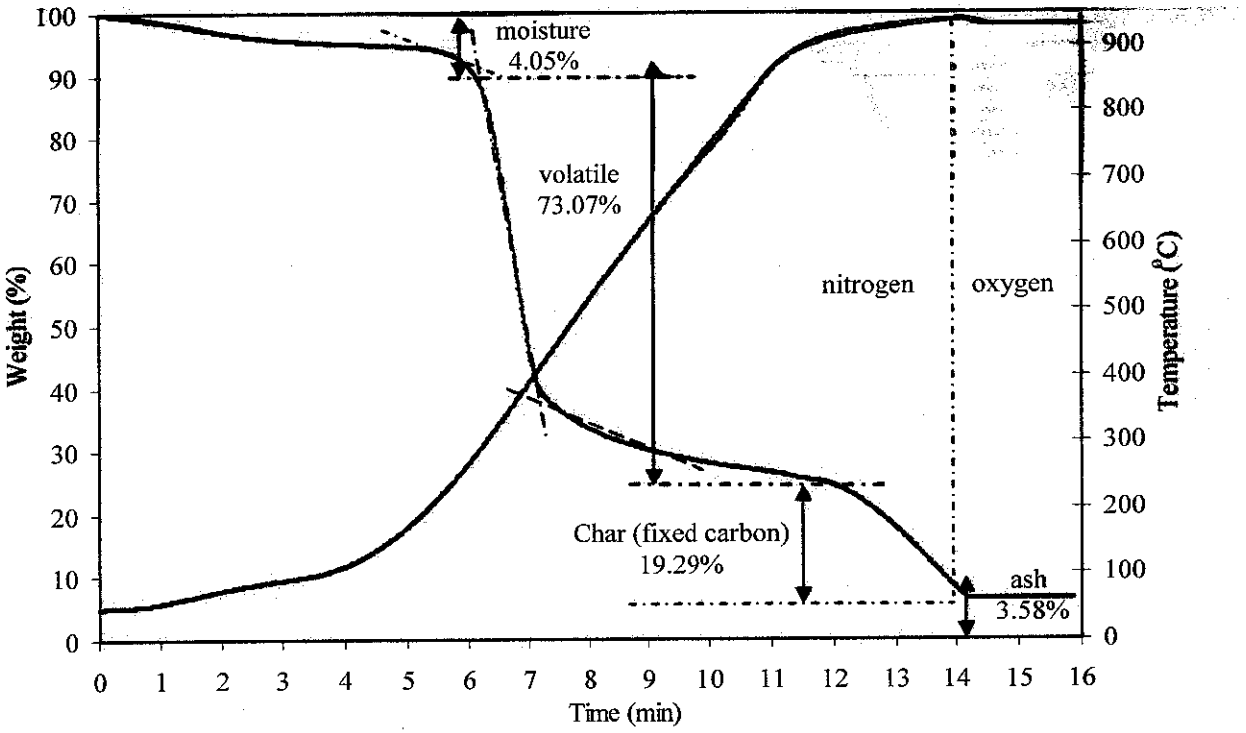


Figure 4.2 Thermogram of thermal gravimetric analysis for PMF size of 355-500 μm.

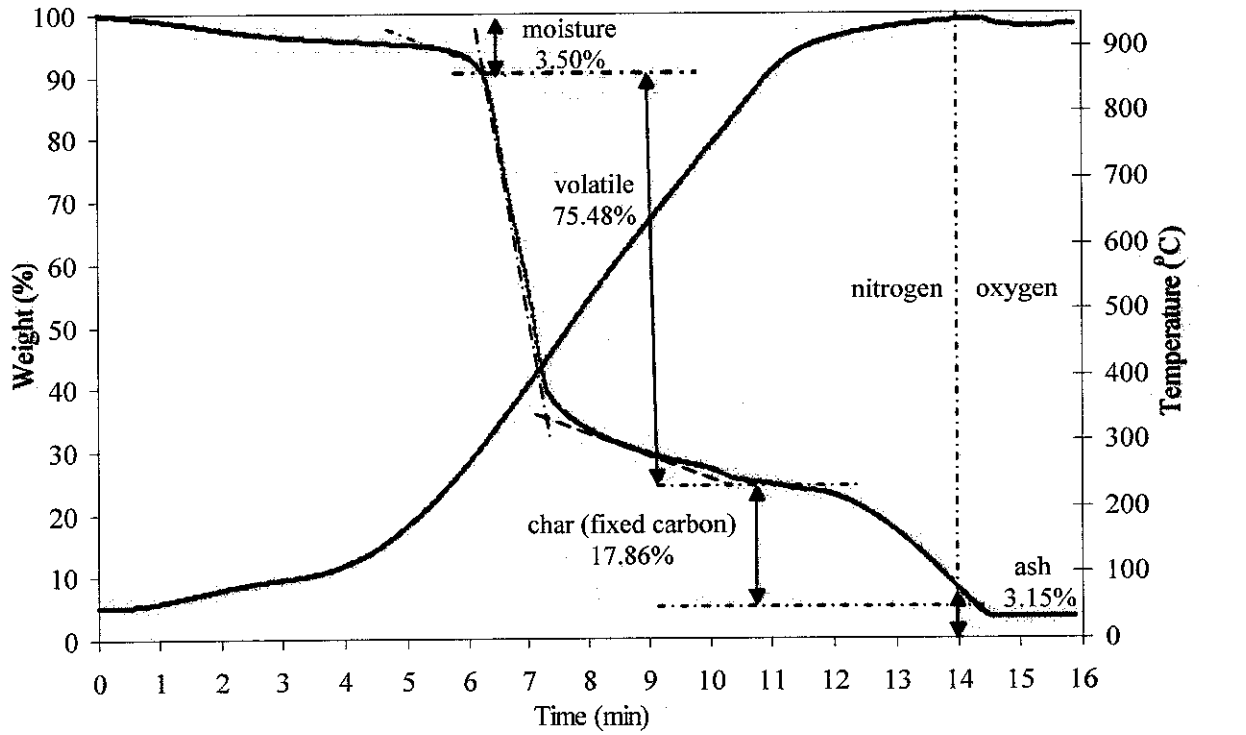


Figure 4.3 Thermogram of thermal gravimetric analysis for PKS size of 355-500 μm.

In this figures, the moisture, volatile matter, fixed carbon and ash were determined through the weight loss of the biomass when subjected to certain conditions. Initially, the biomass was placed under nitrogen atmosphere and heated to 110 °C to measure the moisture content. Then, it was further heated until 900 °C to determine the volatile matters and it was maintained for 5 minutes to determine fixed carbon. The second part of this analysis was performed under oxygen purge (99.9%). The ash content was calculated as the residue remained after the combustion process of fixed carbon has been completed.

Besides, the results of proximate analysis for raw EFB, PMF and PKS with selected size of 355-500 μm for both methods are summarized in Table 4.2. The results have showed that there were slightly difference between the value of moisture, volatile matter, fixed carbon and ash between these two methods. In order to identify deviation between two methods, absolute average deviation (AAD) was introduced as shown in Eq. 4.1. The study had reported that both methods have produced comparable results with the deviation less than 6%. Among this biomass, EFB had the highest moisture and ash content while PKS had the highest volatile matter. In term of fixed carbon, PMF had the highest fixed carbon among them. The proximate analysis of raw oil palm biomass was comparable with the proximate analysis of others raw non-woody biomass as presented in Table 2.3.

Table 4.2 Proximate analysis of raw EFB, PMF and PKS at size of 355-500 μm between ASTM and TGA methods.

Proximate	EFB			PMF			PKS		
Analysis	ASTM	TGA	AAD (%)	ASTM	TGA	AAD (%)	ASTM	TGA	AAD (%)
Moisture (%)	5.18	5.37	3.54	4.16	4.05	2.72	3.30	3.50	5.71
Volatile (%)	73.23	73.96	0.99	74.28	73.07	1.66	75.64	75.48	0.21
Carbon (%)	16.94	16.24	4.31	18.24	19.29	5.44	18.08	17.86	1.23
Ash (%)	4.65	4.42	5.20	3.40	3.58	5.03	2.98	3.15	5.40

$$\text{Absolute Average Deviation (AAD)} = \frac{\text{ASTM method} - \text{TGA method}}{\text{TGA method}} \times 100 \quad (4.1)$$

The study had reported that the raw oil palm biomass contained higher volatile matter than the raw sugarcane bagasse which was 67.31% but lower than the volatile matter of raw reed canary grass which was 82.50%. The study had also found that the volatile matter of raw oil palm biomass was comparable with the volatile matter of bamboo which was in the range of 73 to 74%. In terms of fixed carbon content, the raw oil palm biomass had slightly lower fixed carbon than the raw bamboo and rape stalk. However, the raw oil palm biomass had higher fixed carbon content than the raw reed canary grass which was only 12.10%. Besides, the ash content of raw oil palm biomass was comparable with ash content of raw bamboo which was in the range of 3 to 4%. The study had also found that ash content of raw oil palm biomass was higher than the ash content of raw sugarcane bagasse which was 1.53%.

As compared with coal, the raw oil palm biomass had very low fixed carbon and very high volatile matter. According to Mayoral et. al. (2001), the volatile matter of the coal was within the range of 35 to 45% which was 47 to 50% lower than the volatile matter of the raw oil palm biomass. In addition, the coal contained 40 to 55% of fixed carbon content which was 50% higher than the fixed carbon of the raw oil palm biomass. Therefore, in order to improve the properties of raw oil palm biomass before further thermal conversion processes such as pyrolysis, a pretreatment method such as torrefaction process should be carried out to reduce the volatile matter and increase fixed carbon of the raw oil palm biomass.

In comparison between ASTM and TGA method, the proximate analysis carried out by ASTM method is often tedious and time consuming. For each analysis, ASTM method often took approximately 12 hours to be completed as compared with TGA, being less than 20 minutes. Besides, the amount of fixed carbon of TGA method was calculated by the deduction of moisture, volatile matter and ash per 100%, thus giving manipulated value of fixed carbon in the biomass. Furthermore, ASTM method also required significant amount of sample, which wa around 5 to 10 g. Quite often in research work, the sample that need to be characterized only available in small quantity which is few milligrams, thus causing problems to be analyzed by ASTM method (Mayoral et. al., 2001; Elder, 1983).

Therefore, Elder (1983) had reported that thermal gravimetric analysis was a more convenient alternative that TGA method which originally proposed by Fyan in 1977. The thermal gravimetric analysis technique allowed continuous monitoring of sample weight as function of time or temperature in a sequence of heating steps. The main advantages of thermal gravimetric analysis were rapid determination method which required time less than 20 minutes and the percentage of fixed carbon in the biomass was directly measured from the graph. It also required small sample size which was in the range of 2 to 10 mg. Thus, the study had found that thermal gravimetric analysis was a better method due to its simplicity, accuracy value and rapid method (Yusof et. al., 2008; Heikkinen et. al., 2004; Elder, 1983).

4.2.3 Ultimate Analysis and Gross Calorific Value (GCV)

The ultimate analysis which measured the elemental composition of carbon, hydrogen, oxygen, nitrogen and sulphur and the gross calorific value (GCV) for the raw EFB, PMF and PKS are listed in Table 4.3. In general, they composed 45-47% of carbon content, approximately 5% of hydrogen content, 46-49% of oxygen content with negligible of nitrogen and sulphur content. Meanwhile, their GCV can be estimated as 18 MJ/kg and their O/C ratios were in the range of 1.0 to 1.1. In term of particle size, the results revealed that there were just slight differences between these two particle size ranges. Particularly, for carbon and hydrogen content, their differences were below than 1.0% while for hydrogen content was 0.1-0.3%.

Table 4.3 Ultimate analysis and gross calorific value for raw EFB, PMF and PKS.

Biomass	Ultimate analysis (wt. %)						GCV
	C	H	N	S	O	O/C	(MJ/kg)
EFB size 250-355 μm	45.81	5.15	0.43	0.13	48.48	1.058	17.38
EFB size 355-500 μm	44.60	5.48	0.37	0.18	49.37	1.107	18.04
PMF size 250-355 μm	45.82	5.26	0.57	0.15	48.20	1.052	18.09
PMF size 355-500 μm	46.91	5.44	0.63	0.11	46.92	1.000	18.16
PKS size 250-355 μm	46.76	5.85	0.49	0.12	46.78	1.000	18.16
PKS size 355-500 μm	45.00	6.21	0.42	0.18	48.19	1.071	18.91

4.3 Temperature Profiles of Torrefaction Process

In the present study, the biomass had passed several stages during the torrefaction process as presented in Figure 4.4. The stages are heating, drying, intermediate heating, torrefaction and cooling. Initially, when the biomass was fed into either tube furnace or TGA, it was heated from ambient temperature until the drying stage was reached around 105 °C. At this stage, the temperature was kept constant for 10 minutes where the weight loss of biomass occurred due to the dehydration process. After that, the temperature was increased until around 190°C which called as the intermediate heating stage. During this stage, the weight loss of biomass occurred mainly due to the devolatilization of inorganic volatiles. After that, the temperature was further increased until the desired torrefaction temperature was reached. The torrefaction process started as the temperature reached to 200 °C until the maximum temperature was 300 °C. In the present study, torrefaction time of 120 minutes was selected since it had completely torrefied three types of the oil palm biomass.

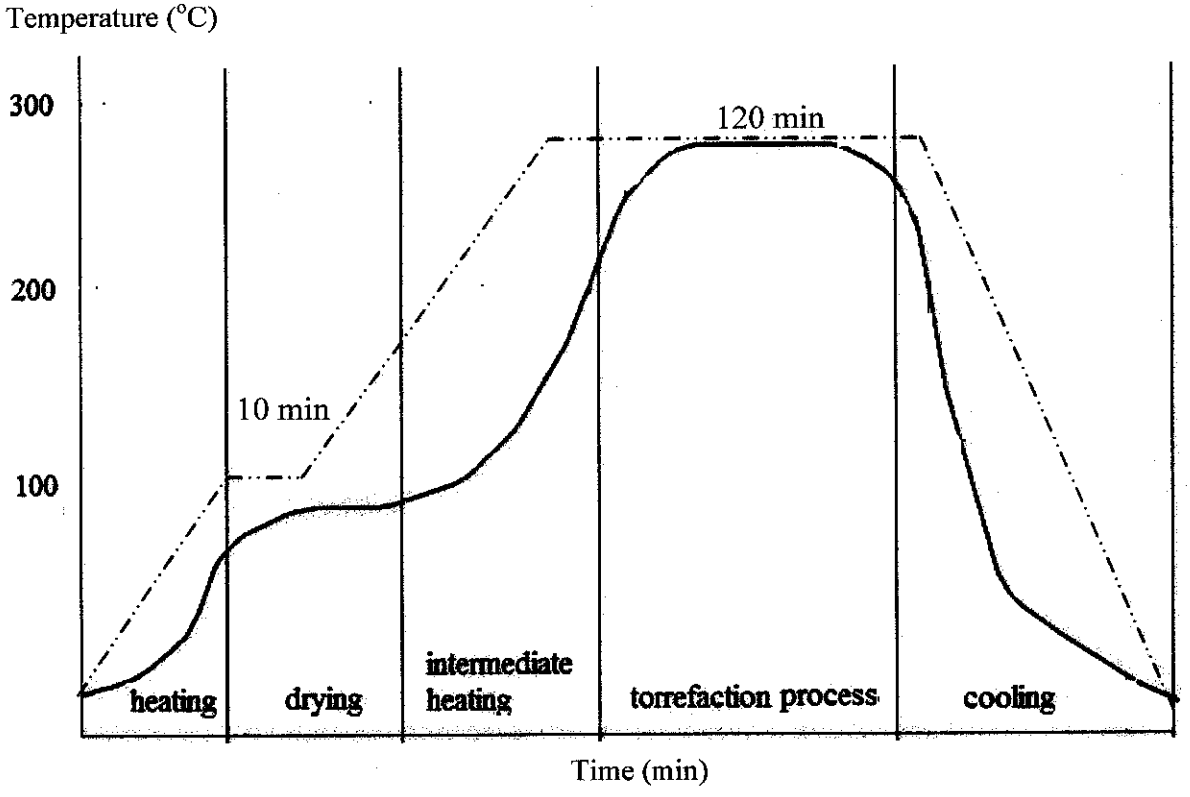


Figure 4.4 Stages involved during torrefaction process.

The example of temperature profile of torrefaction process at 300 °C was represented with the dotted line as shown in the Figure 4.4. Initially, the biomass was heated from ambient temperature until reached at the temperature of 105 °C. The temperature was kept constant for 10 minutes to remove any adsorbed moisture in the biomass. Then, temperature was raised until reached at 300 °C and kept constant for 120 minutes in order to torrefied the biomass completely. The process ended when the system was cooled down to 200 °C again. Finally, the system of TGA or tube furnace was left natural cooling until it reached ambient temperature again.

4.4 Characterization of Torrefied Biomass

4.4.1 Ultimate Analysis and Gross Calorific Value (GCV)

The ultimate analysis and gross calorific value (GCV) for torrefied EFB, PMF and PKS for both particle sizes are summarized in Tables 4.4 to 4.6. During both analyses, the torrefied biomass that produced from torrefaction process in the tube furnace was used. In this analysis, the GCV was in the high heating value (HHV) unit which it was included the latent heat of the vapour emitted from the biomass. As all the biomass were torrefied from mild to severe torrefaction process, an alteration occurred in the elemental composition and GCV, especially for torrefaction process above 260 °C.

In general, the GCV and carbon content in the torrefied biomass had increased with the increasing of torrefaction temperature. These results seem to be in the agreement with the reported literatures (Uemura et. al., 2011; Deng et. al., 2009; Bridgeman et. al., 2008). Thus, the study had revealed that torrefaction process has successfully increased the carbon content and GCV in the torrefied biomass. In contrast, the O/C ratio, hydrogen and oxygen content had decreased with the increasing of torrefaction temperature. The exception was the nitrogen content which it remained less than 2% for all torrefaction conditions. As for sulphur content, at any torrefaction conditions, it always approached to zero.

Table 4.4 Ultimate analysis and gross calorific value for torrefied EFB.

Biomass	Temperature (°C)	Ultimate analysis (wt. %) C	H	N	S	O	O/C ratio	GCV (MJ/kg)
EFB	Raw	45.81	5.15	0.43	0.13	48.48	1.058	17.38
size	200	47.08	4.78	1.45	0.18	46.51	0.988	17.53
250-355 μm	220	47.20	4.56	1.52	0.07	46.65	0.988	17.84
	240	47.68	4.63	1.64	0.10	45.96	0.964	18.85
	260	47.91	4.47	1.76	0.07	45.80	0.956	19.76
	280	50.18	4.25	1.80	0.12	43.66	0.870	21.67
	300	51.31	4.04	1.24	0.04	43.38	0.846	22.59
EFB	Raw	44.6	5.48	0.37	0.18	49.37	1.107	18.04
size	200	47.49	4.79	1.16	0.15	46.41	0.977	18.44
355-500 μm	220	48.33	4.72	1.25	0.08	45.62	0.944	18.90
	240	49.27	4.66	1.27	0.08	44.72	0.908	19.38
	260	49.63	4.51	1.27	0.07	44.53	0.897	19.89
	280	49.84	4.53	1.52	0.10	44.01	0.883	22.18
	300	51.56	4.19	1.43	0.11	42.72	0.828	22.42

Specifically, the carbon content for all torrefied biomass were 47-50% under mild torrefaction process while 48-58% under severe torrefaction process. After mild torrefaction process, the carbon content of PMF was slightly higher than both EFB and PKS. However, after severe torrefaction process, PKS has the highest carbon content followed by PMF and EFB. Hence, the study concluded that depending on the types of biomass, different torrefaction temperature was required to increase the carbon content of the oil palm biomass during torrefaction process. In term of particle size, the carbon content showed that there were slight differences between these two particle size ranges. Particularly, the differences of carbon content were between 0.3-1.5%. Additionally, the study had also made comparison on the carbon of torrefied oil palm biomass with the carbon content of others non-woody biomass as listed in Table 4.7. It can be concluded that the carbon content of torrefied EFB, PMF and PKS were in the good agreement with the carbon content of others torrefied non-woody biomass.

Table 4.5 Ultimate analysis and gross calorific value for torrefied PMF.

Biomass	Temperature (°C)	Ultimate analysis (wt. %) C	H	N	S	O	O/C	GCV (MJ/kg)
PMF	Raw	45.82	5.26	0.57	0.15	48.20	1.052	18.09
size	200	47.60	4.83	1.45	0.04	46.08	0.968	19.13
250-355 μm	220	48.12	4.53	0.97	0.06	46.32	0.963	19.67
	240	50.92	4.47	1.33	0.04	43.24	0.849	19.99
	260	51.73	4.30	1.45	0.17	42.35	0.819	20.21
	280	52.72	3.94	0.85	0.08	42.41	0.804	21.91
	300	52.81	3.64	0.99	0.04	42.52	0.805	23.10
PMF	Raw	46.91	5.44	0.63	0.11	46.92	1.000	18.16
size	200	47.89	4.92	1.23	0.07	45.90	0.958	19.34
355-500 μm	220	47.65	4.73	1.34	0.06	46.22	0.970	19.67
	240	47.87	4.68	1.43	0.14	45.89	0.959	20.09
	260	50.50	4.27	1.56	0.09	43.59	0.863	20.75
	280	51.09	3.91	1.62	0.07	43.32	0.848	22.05
	300	51.50	3.78	1.65	0.04	43.02	0.835	23.73

After severe torrefaction process, the hydrogen content of both EFB and PMF were higher than PKS. Thus, torrefaction process had significantly reduced the hydrogen content of PKS. In addition, the oxygen content of torrefied biomass was in the range of 43 to 46% under mild torrefaction process, while 35 to 44% under severe torrefaction process. Specifically, PMF contained the lowest oxygen content with 43.24% after mild torrefaction temperature, but after severe torrefaction process, PKS had the lowest oxygen content with 35.63%. Therefore, torrefaction process had significantly reduced the oxygen content of PKS. Decreasing of the hydrogen and oxygen content were caused by the formation of CO, CO_2, CH_4, and H_2 during the torrefaction process (Deng et. al., 2009; Bridgeman et. al., 2008). In term of particle size, the hydrogen and oxygen content showed that there were slight differences between these two particle size ranges. Particularly, the differences of the hydrogen and oxygen content were below 1.0%.

Table 4.6 Ultimate analysis and gross calorific value for torrefied PKS.

Biomass	Temperature	Ultimate analysis (wt. %)						GCV
	(°C)	C	H	N	S	O	O/C	(MJ/kg)
PKS size 250-355 μm	Raw	46.76	5.85	0.49	0.12	46.78	1.000	18.16
	200	46.7	5.45	0.88	0.03	46.96	1.006	19.20
	220	46.8	5.38	0.88	0.08	46.89	1.003	19.72
	240	49.2	5.35	0.85	0.06	44.52	0.904	19.86
	260	51.7	4.75	0.48	0.03	43.04	0.832	20.35
	280	57.2	4.66	0.99	0.05	37.13	0.650	21.09
	300	58.7	4.57	1.03	0.03	35.63	0.606	21.54
PKS size 355-500 μm	Raw	45.0	6.21	0.42	0.18	48.19	1.071	18.91
	200	45.9	5.99	0.87	0.03	47.23	1.029	19.48
	220	46.84	5.78	0.91	0.02	46.45	0.992	19.78
	240	46.8	5.63	0.89	0.04	46.63	0.996	20.03
	260	48.2	5.06	0.97	0.13	45.61	0.946	20.83
	280	55.2	4.91	0.89	0.03	39.01	0.707	21.91
	300	55.6	4.71	0.93	0.08	38.73	0.697	22.86

From Table 4.7, the carbon content of torrefied PKS was comparable with the carbon content of torrefied bamboo. The study had found that the torrefied PKS has the highest carbon content which was 58.75% at 300 °C while 58.43% for torrefied bamboo at 280 °C. Besides, the carbon content of torrefied PMF was comparable with the torrefied sugarcane bagasse. For instance, the carbon content of torrefied PMF was 52.72% while 52.81% for torrefied sugarcane bagasse at the temperature of 280 °C. However, the study has found that the carbon content of torrefied EFB was slightly lower than others non-woody biomass. For example, the highest carbon content of torrefied EFB was only 51.31% at 300 °C while the highest carbon content of lucerne was 54.10% at 280 °C. Therefore, the study concluded that the carbon content of torrefied PMF and PKS were comparable with the torrefied sugarcane bagasse and bamboo while the carbon content torrefied EFB slightly lower than others torrefied non-woody biomass.

Table 4.7 Comparison carbon content of torrefied EFB, PMF and PKS with others torrefied non-woody biomass.

Non-woody biomass	Temperature (°C)	Time (h)	Carbon content (%)	References
EFB	220	2.0	47.20	Present study
	240	2.0	47.68	
	260	2.0	47.91	
	280	2.0	50.18	
	300	2.0	51.31	
PMF	220	2.0	48.12	Present study
	240	2.0	50.92	
	260	2.0	51.73	
	280	2.0	52.72	
	300	2.0	52.81	
PKS	220	2.0	46.77	Present study
	240	2.0	49.22	
	260	2.0	51.70	
	280	2.0	57.17	
	300	2.0	58.75	
Reed canary grass	230	0.5	49.30	Bridgeman et. al. (2008)
	250	0.5	50.30	
	270	0.5	52.20	
	290	0.5	54.30	
Bamboo	220	1.0	49.60	Rousset et. al. (2011)
	250	1.0	53.47	
	280	1.0	58.43	
Sugarcane bagasse	230	1.0	48.60	Pach et. al. (2002)
	250	1.0	50.60	
	280	1.0	52.81	
Lucerne	230	1.0	48.70	Chew and Doshi (2011)
	250	1.0	50.70	
	280	1.0	54.10	

Moreover, due to the higher carbon content coupled with lower oxygen content, the O/C ratio was reduced in the torrefied biomass as shown in Table 4.4 to 4.6. These results also seem to be in line with literatures (Uemura et. al., 2011; Bridgeman et. al., 2008). As the torrefaction temperature increased, the O/C ratio of EFB, PMF and PKS were gradually reduced as illustrated in Figures 4.5 to 4.6. Before torrefaction process, O/C ratio of raw biomass was in the range of 1.052 to 1.107. After severe torrefaction process, the O/C ratio had gradually reduced which PKS had the lowest O/C ratio with 0.606 followed by PMF with 0.805 and 0.828 for EFB. Prins et. al. (2006) had reported that torrefaction process was a pre-treatment method that successfully reduced the O/C ratio and had been contributed in the gasification efficiency. Couhert et. al. (2009) had also reported that torrefaction process decreased the O/C ratio of the biomass. Their study had found that during the wood gasification in an entrained flow reactor, the quantity of the syngas produced had been increased significantly.

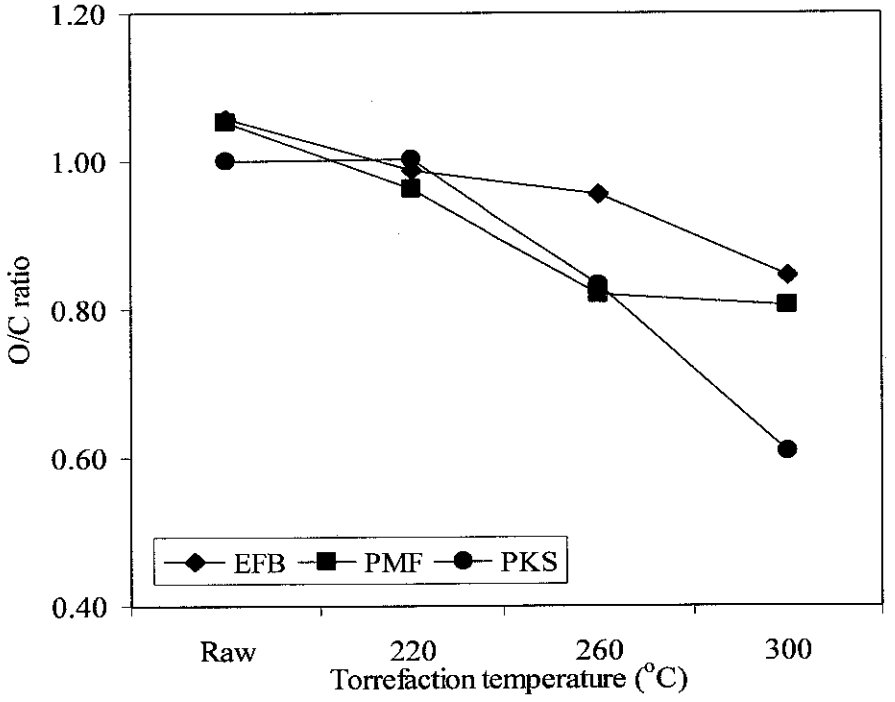


Figure 4.5 Comparison distribution of O/C ratio of torrefied biomass with raw biomass size of 250-355 μm.

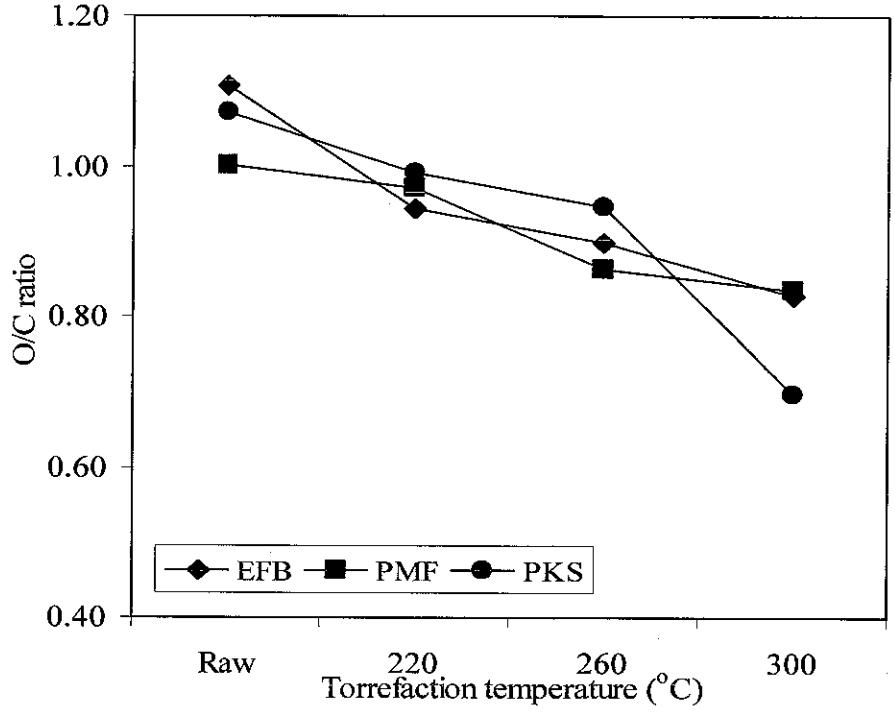


Figure 4.6 Comparison distribution of O/C ratio of torrefied biomass with raw biomass for size of 355-500 μm.

Furthermore, the GCV of torrefied biomass had increased as the torrefaction temperature increased as illustrated in Figures 4.7 and 4.8. The increasing of the GCV was mainly related to the increasing of the carbon content in the torrefied biomass (Uemura et. al., 2011). During torrefaction, biomass loses relatively more oxygen and hydrogen compared to carbon. Subsequently, the calorific value of the torrefied biomass increases. From these figures, it exhibited that the GCV of EFB and PMF were more affected by torrefaction temperature than PKS. This was an indication that both EFB and PMF have undergone more severe decomposition compared to PKS. Once the biomass undergone torrefaction process, the GCV had increased to the range of 20-23 MJ/kg. Under mild torrefaction process, both PMF and PKS have slightly higher GCV with 20.09 MJ/kg and 20.03 MJ/kg; respectively compared to EFB with only 19.38 MJ/kg. However, after severe torrefaction process, PMF had the highest GCV with 23.73 MJ/kg while 23.10 MJ/kg for EFB and 22.86 MJ/kg for PKS. These results had revealed that the GCV was affected by the type of biomass and torrefaction temperature. Therefore, different torrefaction temperatures were required to improve the GCV for each types of biomass.

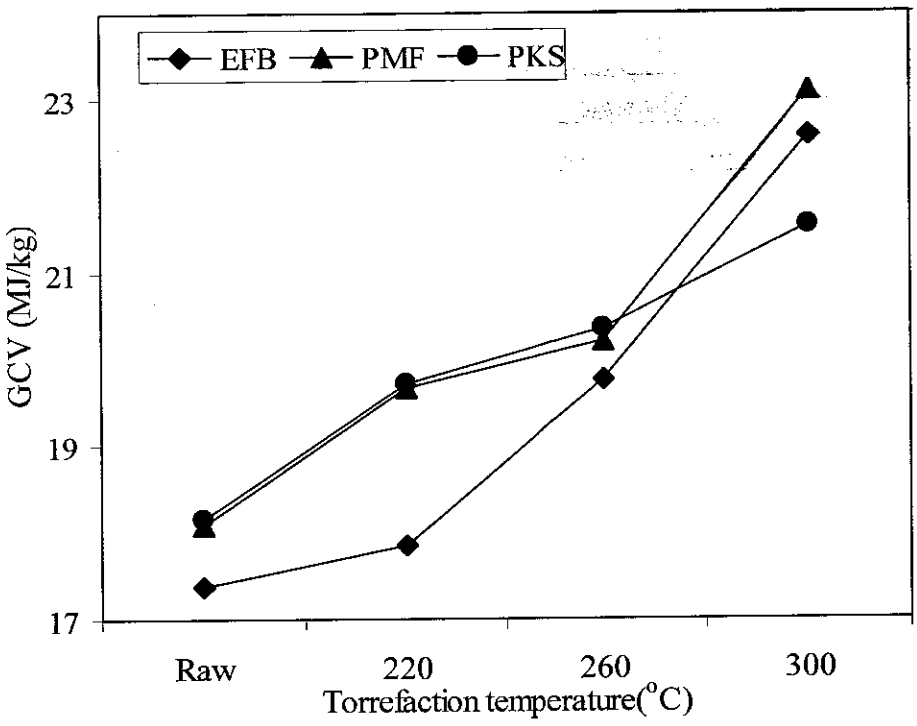


Figure 4.7 Comparison GCV of torrefied biomass with raw biomass for size of 250-355 μm.

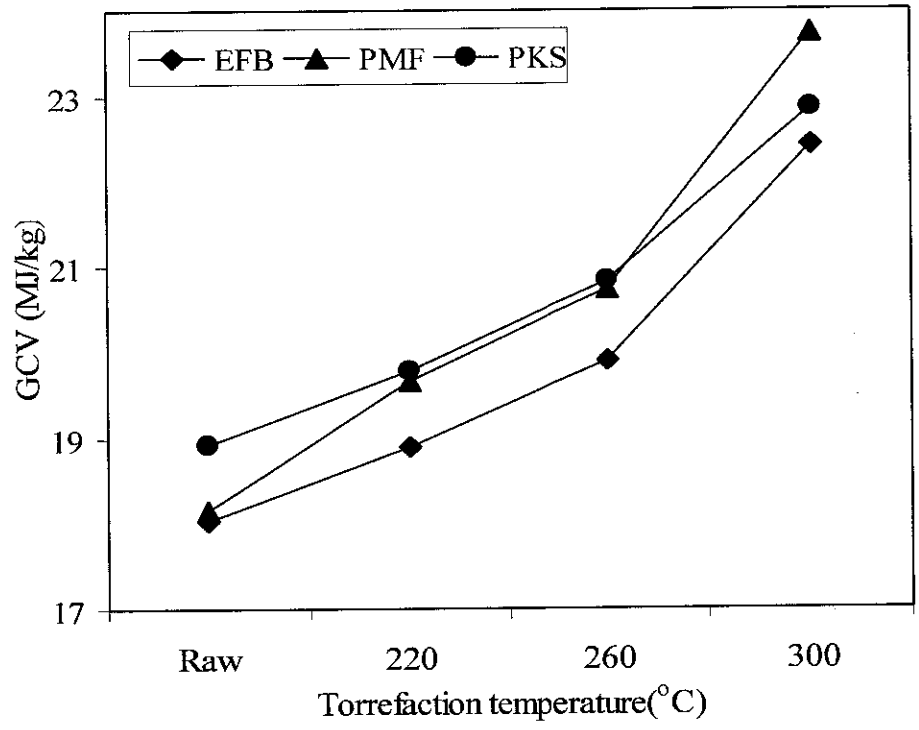


Figure 4.8 Comparison GCV of torrefied biomass with raw biomass for size of 355-500 μm.

Table 4.8 Comparison GCV of torrefied EFB, PMF and PKS with others torrefied non-woody biomass.

Non-woody biomass	Temperature (°C)	Time (h)	GCV (MJ/kg)	References
EFB	220	2.0	17.84	Present study
	240	2.0	18.85	
	260	2.0	19.76	
	280	2.0	21.67	
	300	2.0	22.59	
PMF	220	2.0	19.67	Present study
	240	2.0	19.99	
	260	2.0	20.21	
	280	2.0	21.91	
	300	2.0	23.10	
PKS	220	2.0	19.78	Present study
	240	2.0	20.03	
	260	2.0	20.83	
	280	2.0	21.91	
	300	2.0	22.86	
Reed canary grass	230	0.5	19.50	Bridgeman et. al. (2008)
	250	0.5	20.00	
	270	0.5	20.80	
	290	0.5	21.80	
Bamboo	220	1.0	19.30	Rousset et. al. (2011)
	250	1.0	21.00	
	280	1.0	23.10	
Sugarcane bagasse	230	1.0	17.08	Pach et. al. (2002)
	250	1.0	18.08	
	280	1.0	18.73	
Lucerne	230	1.0	18.69	Chew and Doshi (2011)
	250	1.0	18.75	
	280	1.0	18.89	

Besides, the study had concluded that the GCV of torrefied EFB, PMF and PKS were in line with the GCV of others non-woody torrefied biomass as presented in Table 4.8. The study had found that the GCV of torrefied PMF was comparable with the GCV of torrefied bamboo. For instance, the GCV of torrefied PMF was 19.67 MJ/kg while 19.30 MJ/kg for torrefied bamboo at the temperature of 220 °C. Moreover, the GCV of torrefied PKS was comparable with the GCV of torrefied reed canary grass. For instance, the GCV of torrefied PKS was 20.83 MJ/kg at the temperature of 260 °C, while 20.80 MJ/kg for torrefied reed canary grass at 270 °C. However, the GCV of the torrefied sugarcane bagasse and lucerne were lower than the torrefied EFB, PMF and PKS. The GCV of the torrefied sugarcane bagasse and lucerne were in the range of 17.08 to 18.89 MJ/kg; respectively. Thus, the study had found that the GCV of torrefied oil palm biomass were comparable with torrefied bamboo and reed canary grass and it was slightly higher than the GCV of torrefied sugarcane bagasse and lucerne.

4.4.2 Weight Loss Distributions

The weight loss distributions of torrefaction process for both particle sizes of EFB, PMF and PKS which had been monitored by TGA are illustrated in Figures 4.9- 4.14. From these figures, it can be observed that the weight loss was influenced by the torrefaction temperature. According to Chen and Kuo (2010a), they have studied two torrefaction conditions. They proposed that mild torrefaction process was at 240 °C while severe torrefaction process was at 275 °C. Thus, in the present study, it has been suggested that torrefaction at 200-240 °C was considered as mild torrefaction process while torrefaction at 260-300 °C, was considered as severe torrefaction process. Furthermore, they also reported that the torrefaction process of biomass can be divided into two main stages (Chen and Kuo, 2010a). The present study had also found that torrefaction process of oil palm biomass can be divided into two stages which can be observed through the weight loss distributions as presented in Figures 4.9 to 4.14. The first stage was mainly due to the dehydration at the temperature below 105 °C, where the moisture was released from the biomass. During this stage, the weight reduction was observed within the range of 3 to 5%.

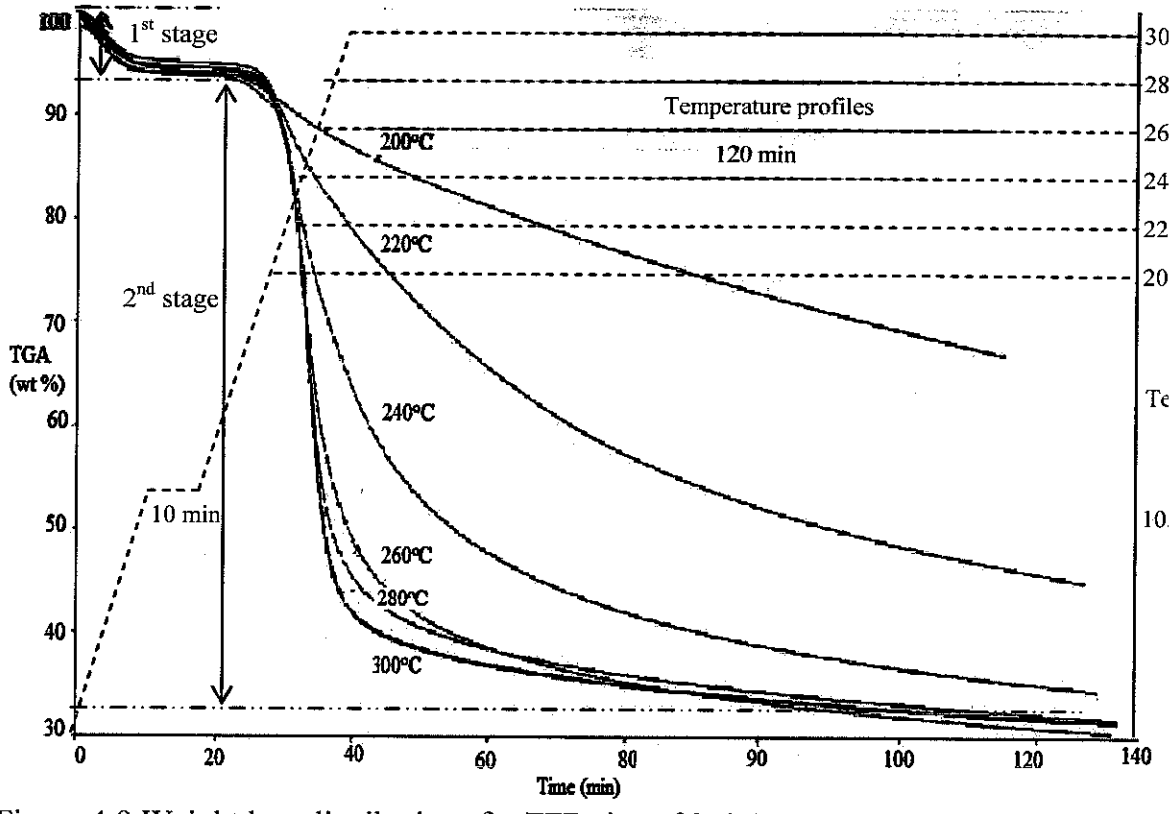


Figure 4.9 Weight loss distributions for EFB size of 250-355 μm.

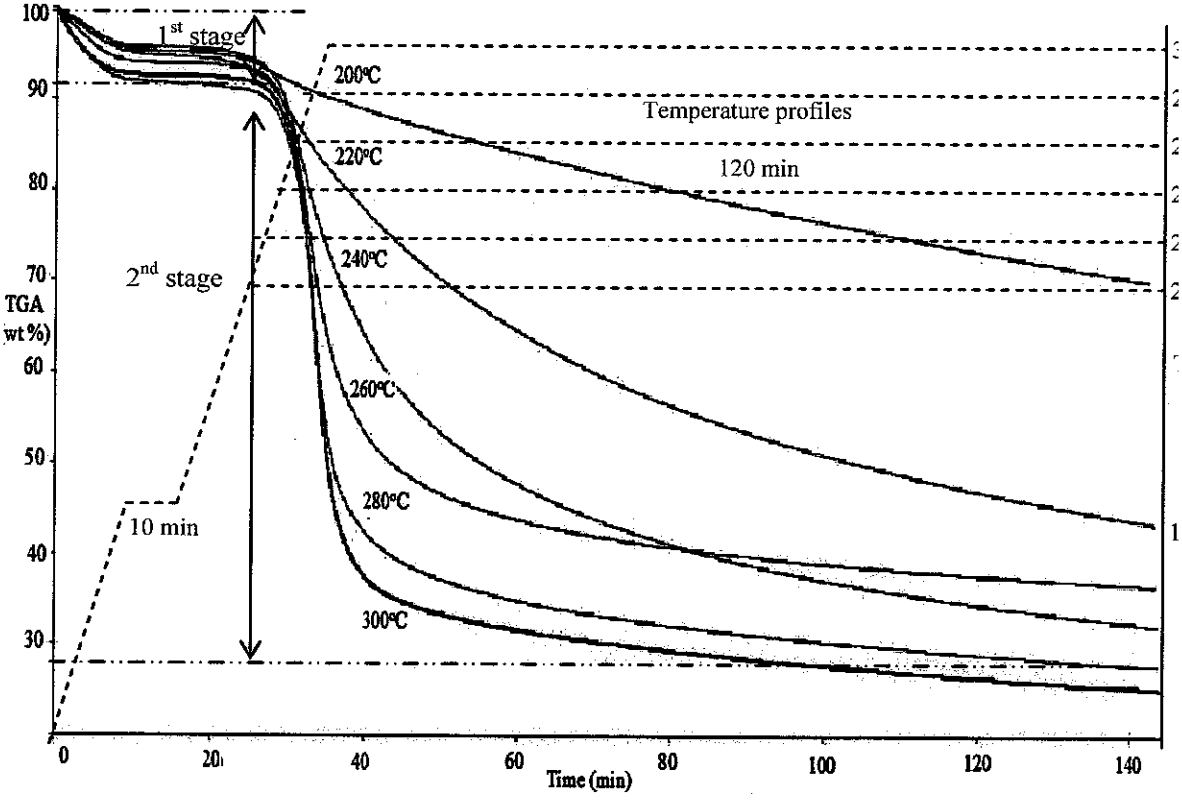


Figure 4.10 Weight loss distributions for EFB size of 355-500 μm.

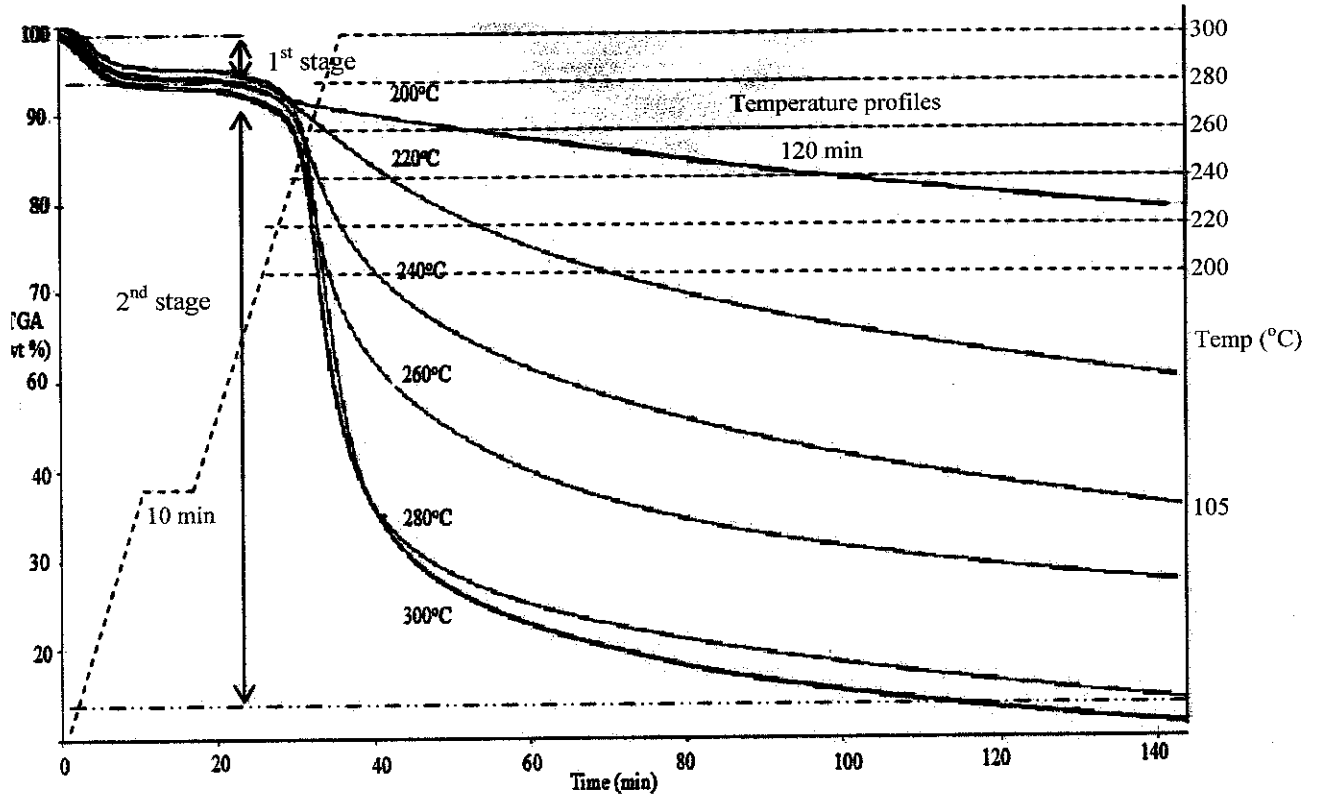


Figure 4.11 Weight loss distributions for PMF size of 250-355 μm.

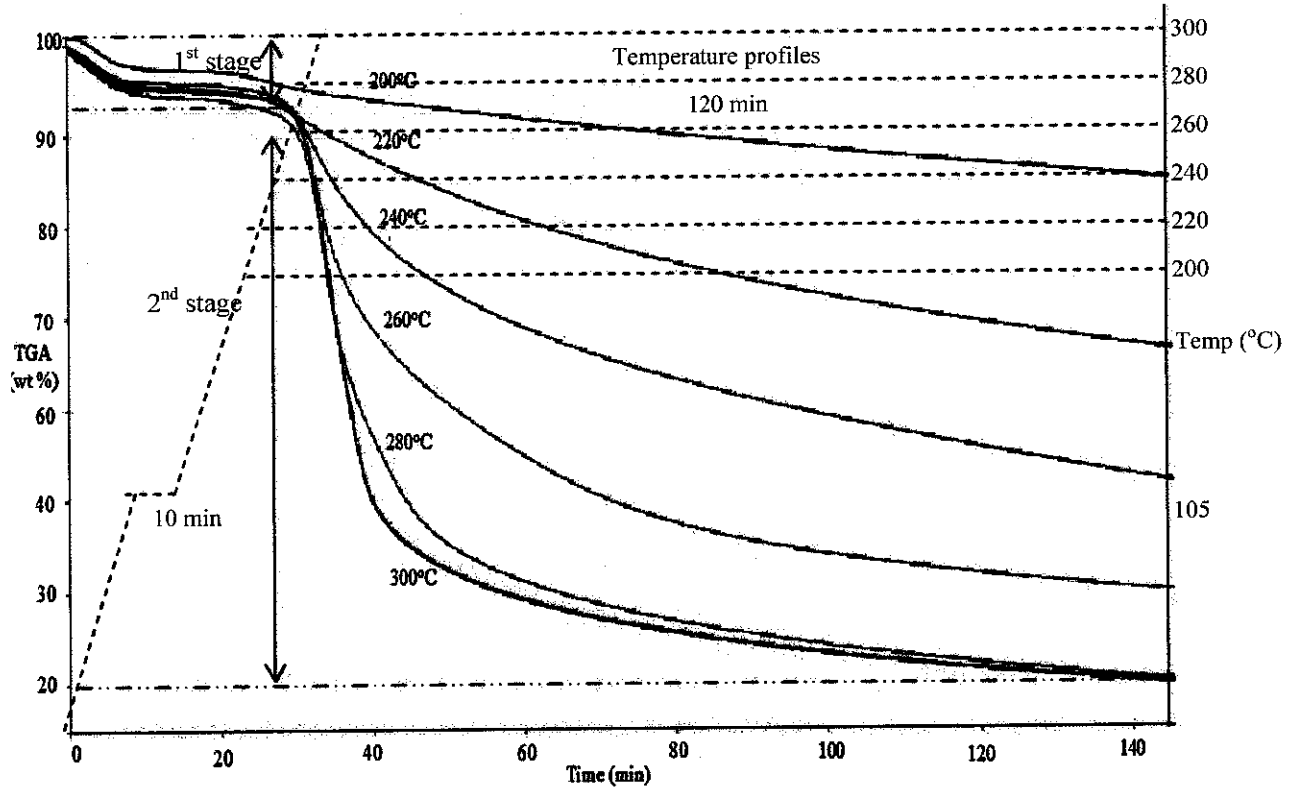


Figure 4.12 Weight loss distributions for PMF size of 355-500 μm.

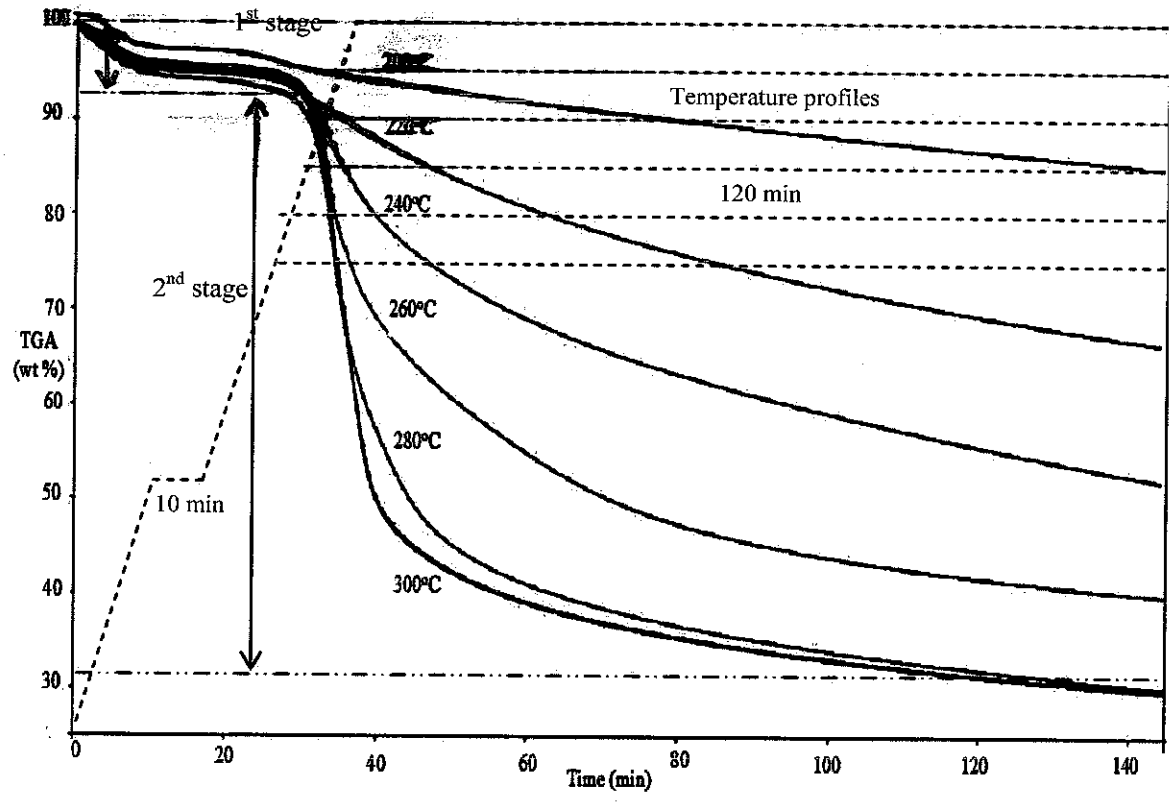


Figure 4.13 Weight loss distributions for PKS size of 250-355 μm.

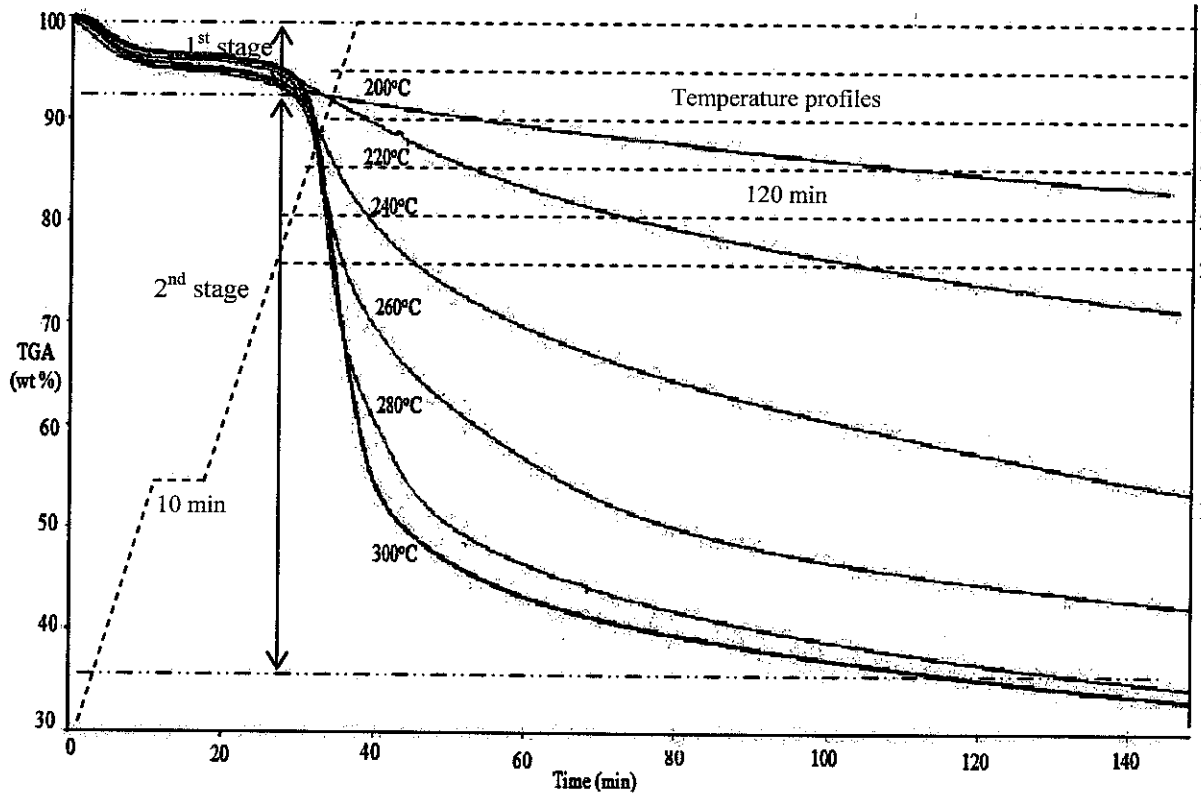


Figure 4.14 Weight loss distributions for PKS size of 355-500 μm.

In the second stage, the decomposition reaction was took place at 200 to 300 °C, where the significant weight reduction had been observed for all types of biomass. During this stage, the weight reduction within the range of 45-55%, depending on the final torrefaction temperature and type of biomass used. These two stages were clearly demonstrated through the weight loss distributions for each torrefied biomass as shown in Figures 4.9 to 4.14. Besides, the slopes of the curves were considered as the decomposition rate of the biomass during torrefaction process. From the figures, the slopes of curves were increased as the torrefaction temperature increased. Thus, the study had found that for each types of biomass, the decomposition rate was higher at the high level of torrefaction temperatures, especially at the temperature above 260 °C. However, after 140 minutes of torrefaction time, the curves of weight loss distributions for all types of biomass were remained stable which indicating that the decomposition biomass was almost completed.

The weight remaining for each types of biomass for every final torrefaction temperatures are listed in Table 4.9. The study had found that after the biomass undergone mild torrefaction process, 41.45% of EFB, 49.06% of PMF and 56.98% of PKS remained at the temperature of 240 °C. However, after severe torrefaction process, only 28.80% of EFB, 32.76% of PMF and 36.42% of PKS remained at the temperature of 300 °C.

Table 4.9 Biomass weight remaining (wt. %) for every torrefaction temperatures.

Torrefaction Temperature (°C)	Biomass weight remaining (wt. %)					
	EFB*	EFB**	PMF*	PMF**	PKS*	PKS**
200	72.66	74.56	87.73	88.18	85.18	81.26
220	49.75	48.22	70.91	75.29	64.76	64.72
240	40.63	42.26	50.82	47.31	55.65	58.32
260	37.24	36.21	44.35	46.42	43.86	37.34
280	28.29	31.23	35.47	39.49	37.09	35.52
300	27.90	29.86	33.38	32.14	35.73	36.42

* size of 250-355 μm; ** size of 355-500 μm

Due to the lowest weight remained in EFB, the decomposition rate of EFB was the most affected during torrefaction process followed by PMF and PKS. The lowest weight remained of EFB might be attributed by the high content of hemicellulose in EFB compared to others. Particularly, high content of hemicellulose can enhance the decomposition rate during torrefaction process (Chen and Kuo, 2010a; Almeida et. al., 2010). Hence, due to higher hemicellulose content in EFB, the reactivity of decomposition rate was higher than both PMF and PKS. Hence, it has contributed in higher weight loss for torrefaction process of EFB. Besides, PKS was the most difficult to be decomposed during torrefaction process. The study suggested that high lignin content of PKS had contributed in lower decomposition rate of PKS (Almeida et. al., 2010). Hence, the weight remained for PKS was the highest after 300 °C, compared to others. Therefore, the decomposition rate of EFB, PMF and PKS were affected by the composition of hemicellulose, cellulose and lignin. For the effect of particle sizes, the study had found that there were slight significant differences between the particle size of 250-355 μm and 355-500 μm. Thus, it can be suggested that the weight loss distributions during torrefaction process were not clearly affected especially for the particle sizes below 500 μm.

4.4.3 Mass Loss Analysis

Mass loss (*ML*) of torrefied biomass which produced from the torrefaction process in the tube furnace was calculated by the following equation:

$$ML = \frac{M_0 - M_t}{M_0} \times 100 \qquad (4.2)$$

where M_o was the mass biomass before torrefaction process while M_t was the mass after torrefaction process. The mass loss for biomass size of 250-355 μm and 355-500 μm are presented in Figures 4.15 to 4.16. The study had reported that as the torrefaction temperature increased, the mass loss also gradually increased which was indicating that mass loss was temperature dependant. In particular, the mass loss for EFB, PMF and PKS were in the range of 11-57%, 20-55% and 10-39%; respectively. After mild torrefaction process, the study had found that the mass loss of EFB was more than 23%, 25% for PMF whereas more than 14% for PKS.

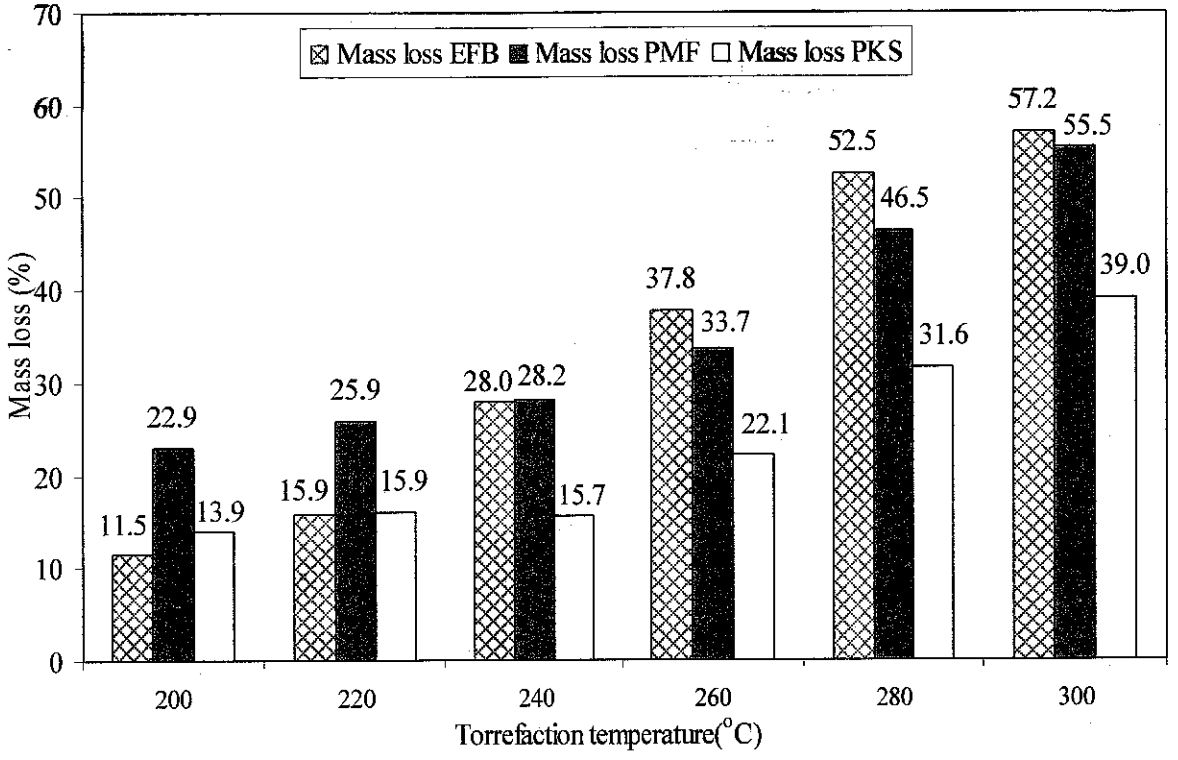


Figure 4.15 Mass loss for biomass size of 250-355 μm.

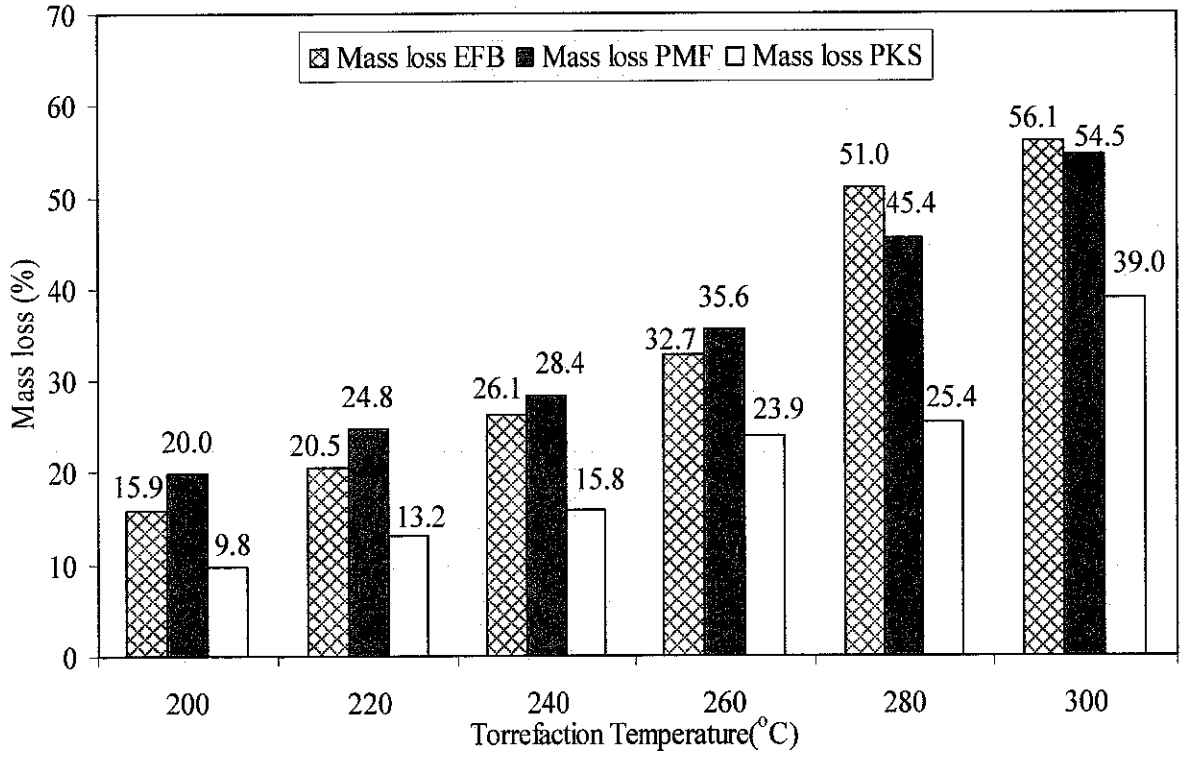


Figure 4.16 Mass loss for biomass size of 355-500 μm.

In comparison, after severe torrefaction process, higher mass loss occurred especially for EFB and PMF. The mass loss for EFB was in the range of 33-57% while 36-56% for PMF. Meanwhile, the mass loss of PKS was lower than both EFB and PMF which only ranging between 22-39%. As comparison, at the torrefaction temperature of 300 °C, the mass loss of both EFB and PMF was 56% whereas only 39% for PKS. Therefore, the study had found that PKS has the lowest mass loss compared to both PMF and EFB after severe torrefaction conditions. It also indicated that only 44% of mass retained in the EFB and PMF after severe torrefaction conditions. On the other hand, after severe torrefaction process of PKS, around 61% of mass retained. Thus, at any torrefaction temperature, both EFB and PMF have higher mass loss than PKS, reflecting that both these biomass were more significantly affected by torrefaction temperature.

These observations might be related to the decomposition temperature of hemicellulose, cellulose and lignin for each oil palm biomass. PKS had the highest lignin content which having slow decomposition reactivity that gradually started from 250 to 500 °C (Chen and Kuo, 2010a). Therefore, the mass loss of PKS was the lowest due to less drastic of decomposition during the torrefaction process. The lignocellulosic analysis also had been reported that the EFB and PMF contained higher amount of hemicellulose. Thus, it had contributed in the higher mass loss for both of EFB and PMF during torrefaction process. The hemicellulose decomposition had been started at the lower temperature which 150 °C and its decomposition almost intense at the temperature of 280 to 300 °C (Chen and Kuo, 2010a). In comparison to the cellulose and lignin, hemicellulose is the most sensitive component when submitted to high temperature environment due to its lower thermal stability (Almeida et. al., 2010). Therefore, it was very noteworthy that the decomposition temperatures of hemicellulose, cellulose and lignin have significant impact on the mass loss of torrefaction oil palm biomass.

4.4.4 Potential of Mass Loss as Indicator of Torrefaction Severity

In the present study, the mass loss had been suggested as an excellent indicator for the severity of torrefaction conditions. Almeida et. al. (2010) had also reported that mass loss can be a synthetic indicator for the severity of torrefaction process. Thus, based on this previous study, mass loss was also proposed to be a good indicator the severity of torrefaction process in the present study. The carbon content and gross calorific value particle sizes of 355-500 μm were randomly selected as the trial parameters. Besides, three different torrefaction temperatures namely 220, 260 and 300 °C were chosen in order to study the relationship of mass loss between carbon content and gross calorific value. The plotted graphs of gross calorific value as function of mass loss and carbon content as function mass loss for EFB, PMF and PKS size 355-500 μm were presented in Figures 4.17 to 4.22.

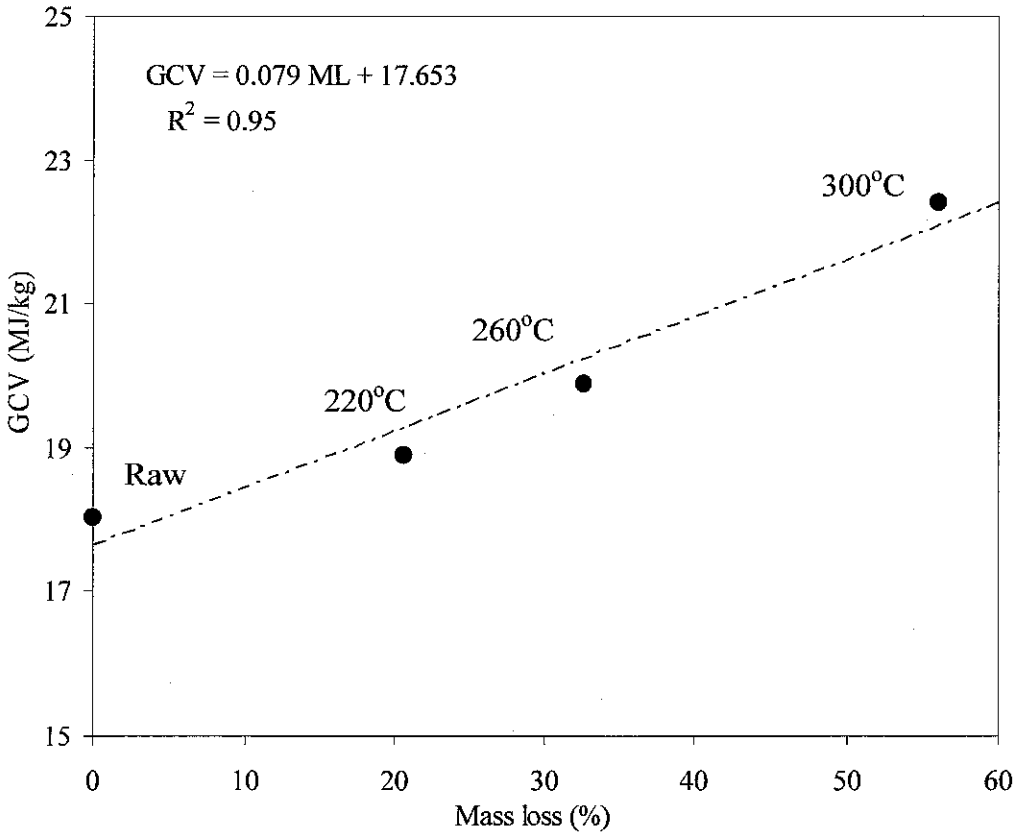


Figure 4.17 GCV as function of mass loss EFB size 355-500 μm.

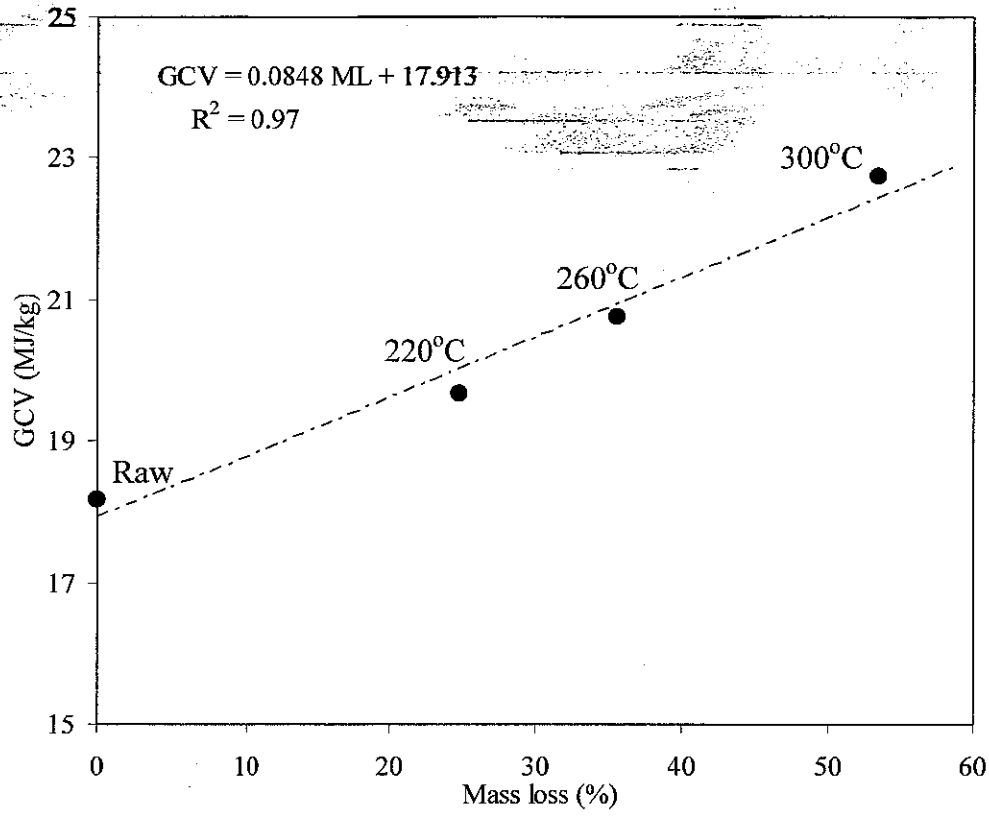


Figure 4.18 GCV as function of mass loss PMF size 355-500 µm.

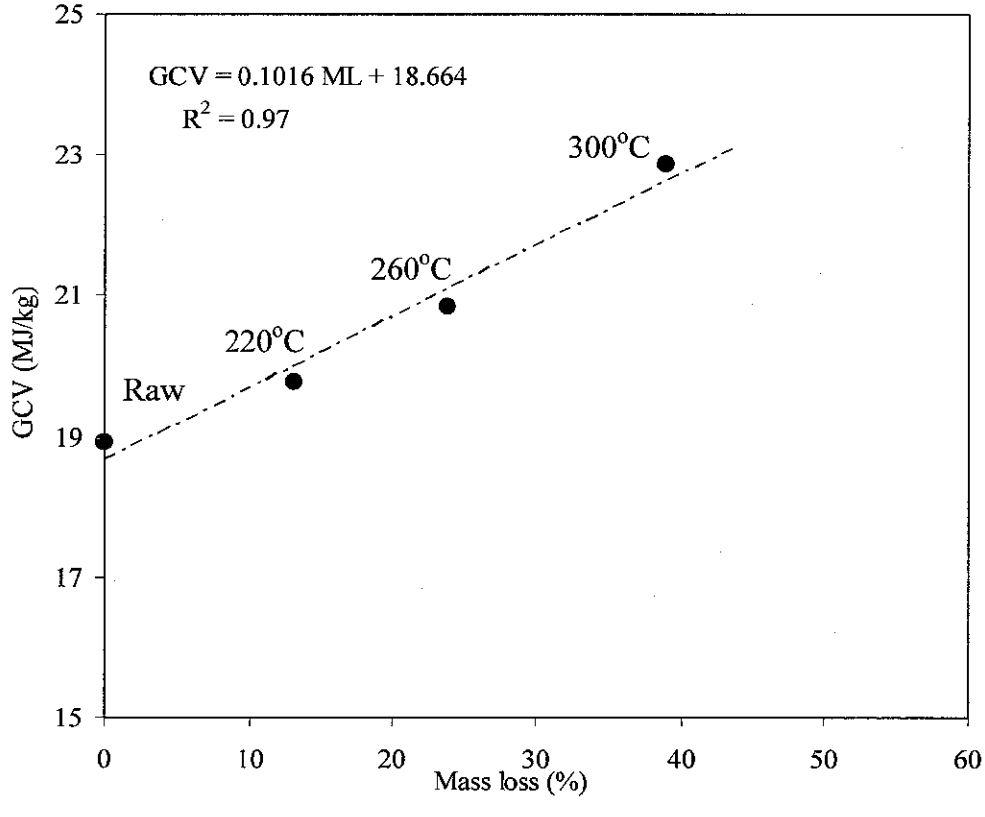


Figure 4.19 GCV as function of mass loss PKS size 355-500 µm.

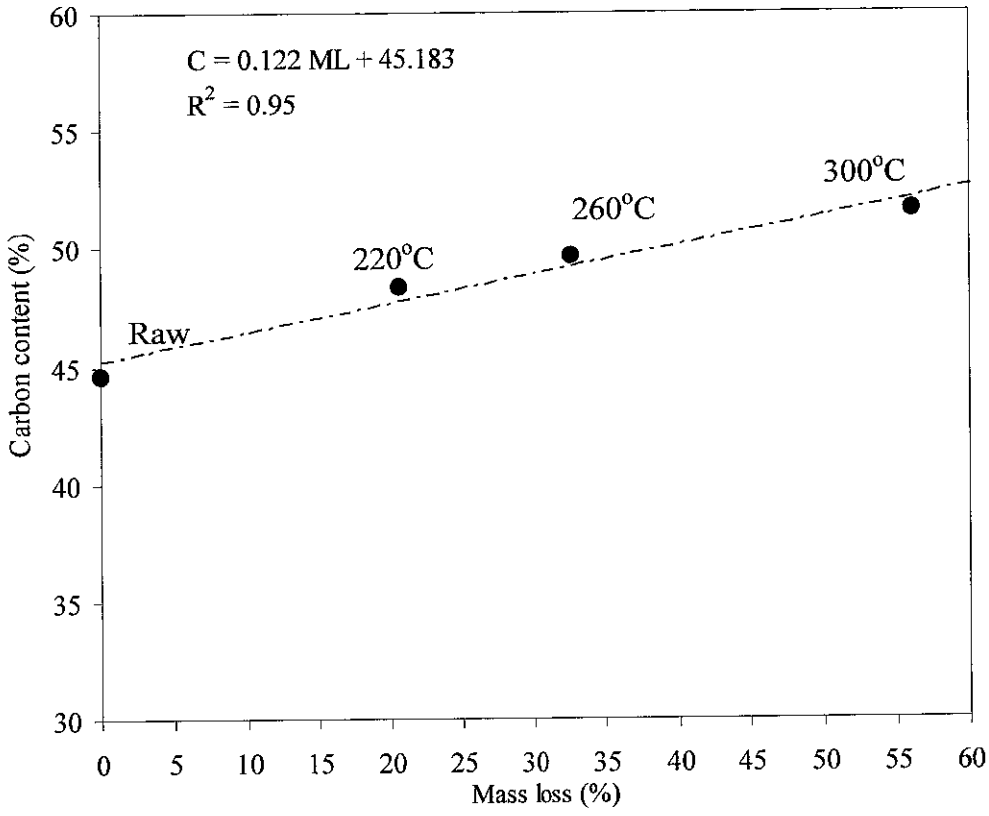


Figure 4.20 Carbon content as function of mass loss EFB size 355-500 μm.

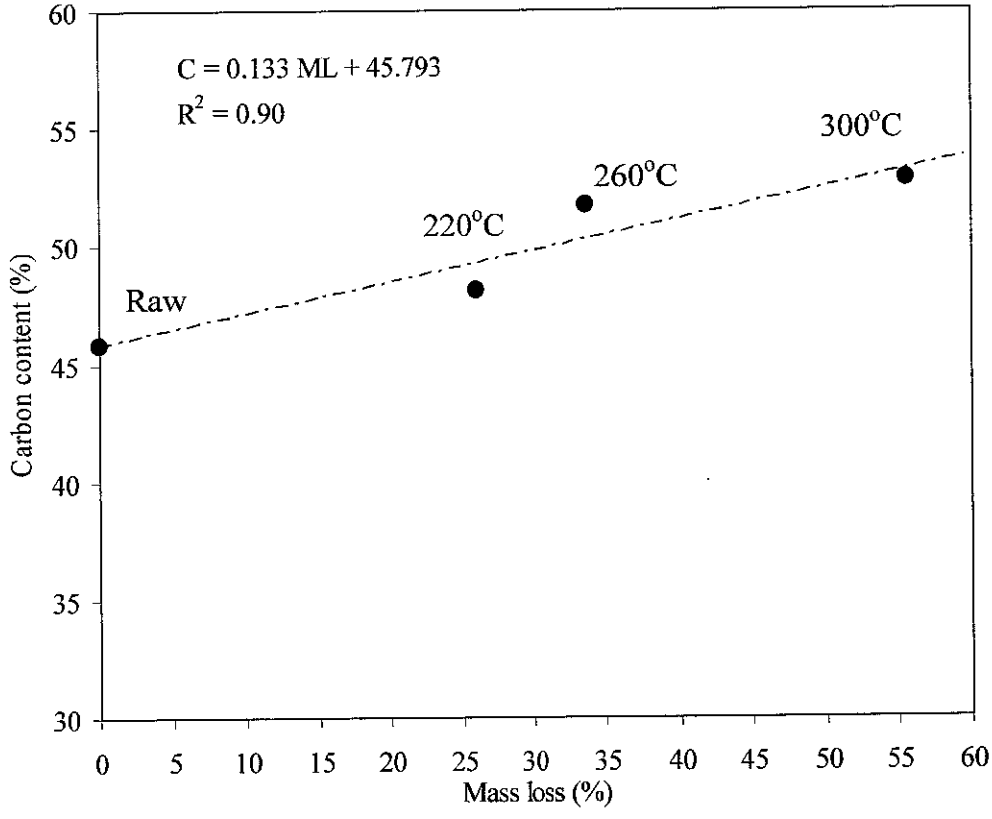


Figure 4.21 Carbon content as function of mass loss PMF size 355-500 μm.

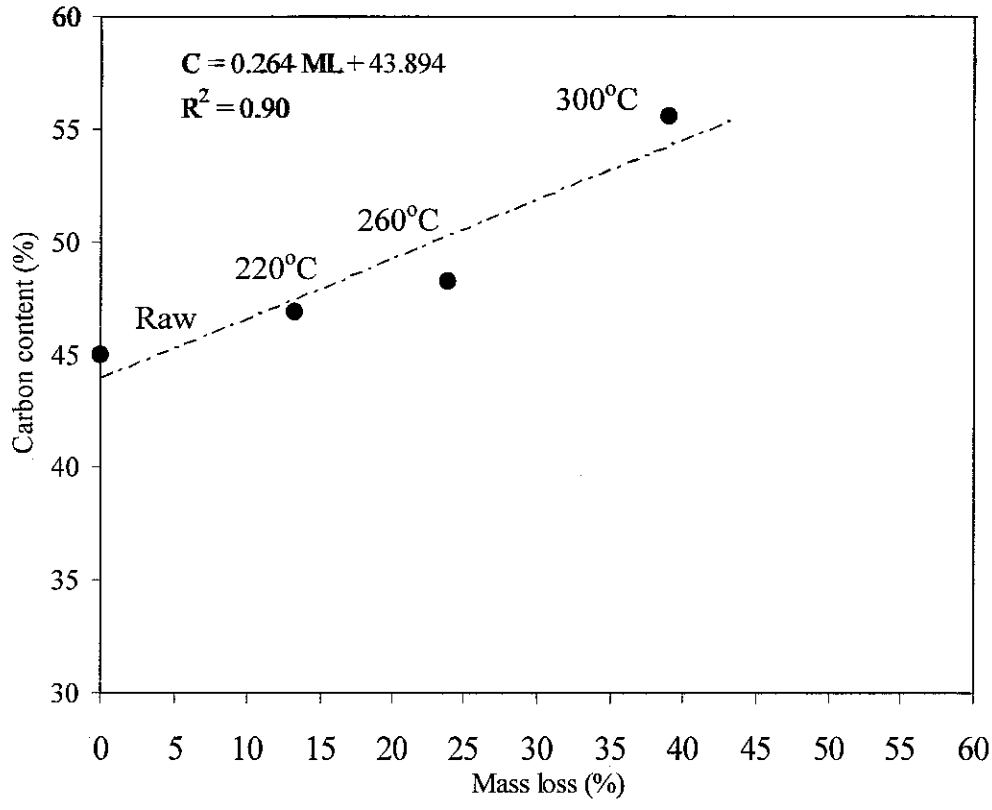


Figure 4.22 Carbon content as function of mass loss PKS size 355-500 μm.

From the studies, it had been found that there were good correlations between the mass loss with the carbon content and the mass loss with the gross calorific value. In particular, the graph of GCV as function of mass loss have demonstrated linear relationship with $R^2 = 0.95$ for EFB, $R^2 = 0.97$ for PMF and $R^2 = 0.97$ for PKS. Meanwhile, the graph of carbon content as function of mass loss also have showed linear relationship with $R^2 = 0.95$ for EFB, $R^2 = 0.90$ for PMF and $R^2 = 0.90$ for PKS. These good correlations that have been showed for these three torrefied oil palm biomass clearly showed that the mass loss was a good indicator for the torrefaction severity. Furthermore, the GCV and carbon content were important parameters that need to be considered in order to study the relationship between the mass loss with torrefaction severity. Therefore, the study had suggested that mass loss was a useful indicator for the torrefaction severity.

4.4.5 Mass and Energy Yields

In biomass energy applications, torrefaction aims for the production of a fuel has improved properties compared to the raw biomass. However, this should be achieved without losing too much chemical energy to the volatile products during the process. Hence, the mass and energy yield were considered to be crucial parameters as an indicator of torrefaction. In the present study, the gross calorific value (GCV) had been used to calculate the energy yield. The GCV indicated the energy content that was released when the solid fuel is burnt. The mass and energy yield (Y_{mass} and Y_{energy}) of torrefied biomass that produced from tube furnace were defined as in Eqs. 4.3 and 4.4 (Uemura et. al., 2011). The mass and energy yields for EFB, PMF and PKS at size of 250-355 μm and 355-500 μm are illustrated in Figures 4.23 to 4.25.

$$Y_{mass}\ (\%) = (\text{mass after torrefaction} / \text{mass before torrefaction}) \times 100 \quad (4.3)$$

$$Y_{energy}\ (\%) = (Y_{mass} \times (GCV_{torrefied\ biomass} / GCV_{raw\ biomass}) \times 100 \quad (4.4)$$

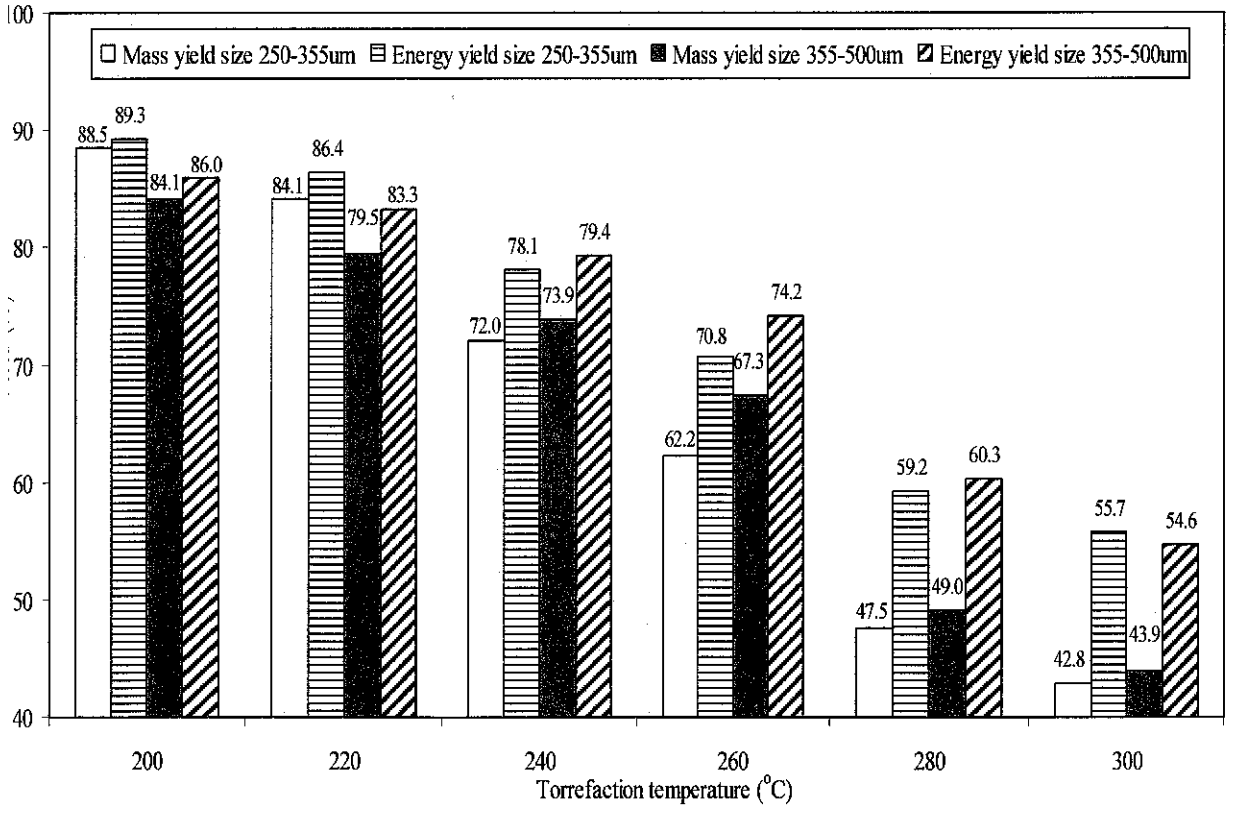


Figure 4.23 Mass and energy yield for EFB as function of torrefaction temperature

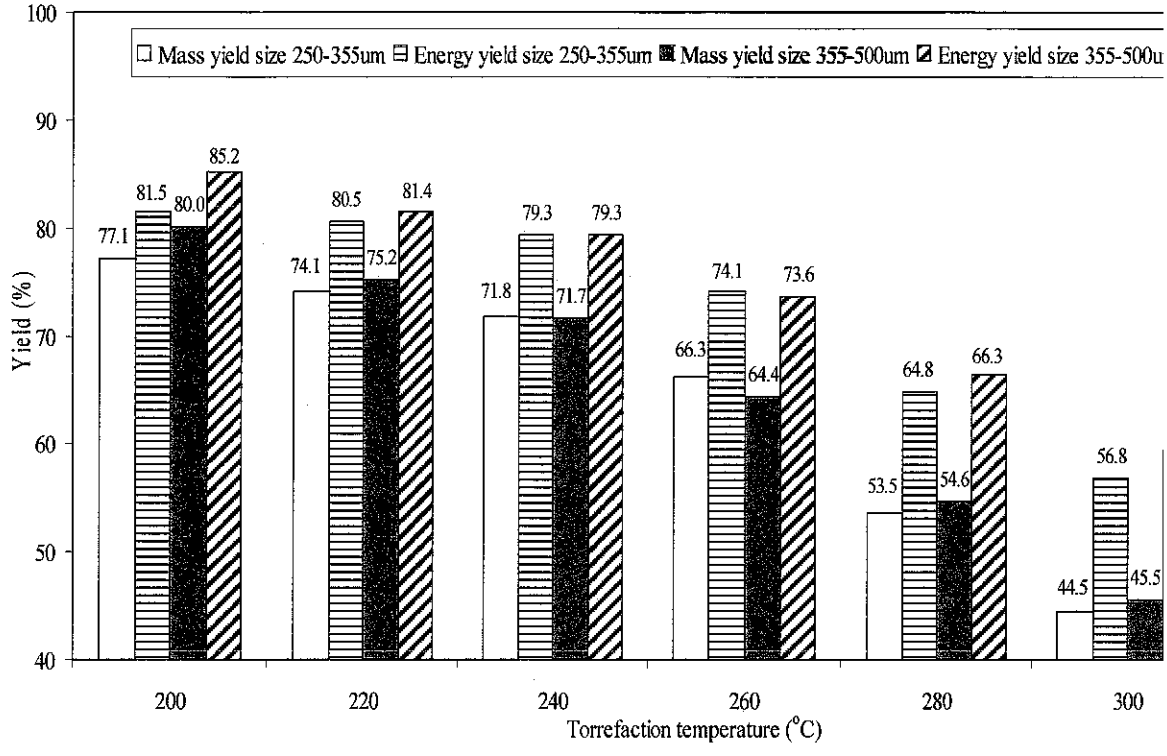


Figure 4.24 Mass and energy yield for PMF as function of torrefaction temperature.

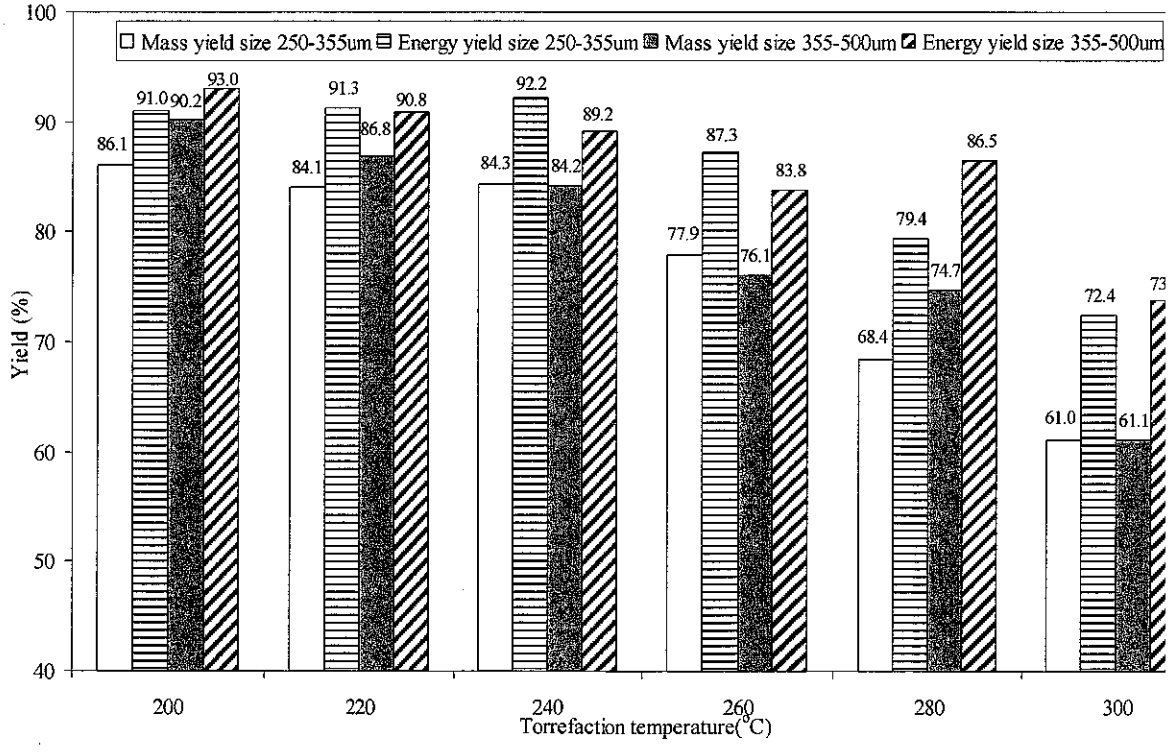


Figure 4.25 Mass and energy yield for PKS as function of torrefaction temperature.

As the torrefaction temperature increased, the mass and energy yield decreased steadily. These observations were also in the agreement from the literatures (Uemura et. al., 2011; Bridgeman et. al., 2008). The study had found that the decreasing ratio of mass yield was depending on the types of biomass where EFB has the highest decreasing ratio followed by PMF and PKS. In particular, there were two main causes for the decreasing in the mass of torrefied biomass (Uemura et. al., 2011). One is moisture loss and secondly, due to thermal decomposition to form gaseous products. While for severe torrefaction process, the decrease is mainly attributed by the decomposition of hemicellulose. Additionally, the study has suggested that the lower mass yield of EFB than PMF and PKS might be related to high mass loss in EFB. Chen and Kuo (2010a) and Almeida et. al. (2010) have also reported that the composition hemicellulose, cellulose and lignin of the feedstock had affected the torrefaction process. They reported that the decomposition rate of the torrefied biomass increased as the hemicellulose content increased. Therefore, due to higher hemicellulose content in EFB and PMF, the decomposition rates for both of them were higher than PKS. Hence, the study suggested that the mass yield depending on the composition of hemicellulose, cellulose and lignin of the feedstock.

Moreover, the study reported that the energy yield of EFB, PMF and PKS decreases as the torrefaction temperature increases. The energy yield of EFB was in the range of 55-89%, with the highest values at the temperature of 200 and 220 °C. Meanwhile, the energy yield of PMF was in the range of 57-85%, with the highest values at the temperature of 200 and 220 °C. In general, the lower energy yield of EFB and PMF were mainly caused by the poor mass yield as presented in Figures 4.23 to 4.25 (Uemura et. al., 2011). Moreover, the energy yield produced of PKS was in the range of 72-93%, with the highest value at 200 to 240 °C. In comparison with the energy yield of both EFB and PMF, PKS always had higher energy yield either after light or severe torrefaction process. Thus, the study had suggested that the energy yield of PKS was the least affected by the torrefaction temperature compared to both EFB and PMF.

Specifically, the energy yield of EFB and PMF only retained around 78-79% while 90% for PKS at 240 °C. However, the energy yield of EFB and PMF were drastically decreased to around 56-58% after 300 °C. Unlike both EFB and PMF, the energy yield of PKS has successfully retained at around 80-86% at 280 °C. However, there was slightly reduction in the energy yield of PKS to around 73% at 300 °C. This observation might be caused by further decomposition of hemicellulose and cellulose in PKS. Therefore, EFB and PMF should be only torrefied under mild torrefaction process to preserve the energy yield above than 78%. Meanwhile, PKS can be torrefied under severe torrefaction process up to 280 °C in order to obtain energy yield around 80-86%. Thus, the study concluded that the mass and energy yield were depending on the torrefaction temperature and biomass types. In addition, torrefaction process at 300 °C was not recommended caused it produced very low energy yield which less than 70% and produced low mass yield which less than 45%.

The study had also made comparable comparison of the mass and energy yield of torrefied EFB, PMF and PKS with others torrefied non-woody biomass as listed in Table 4.10. From the table, the mass yield of torrefied non-woody biomass was in the range of 43-92% while the energy yield was in the range of 56-96%. The study reported that the mass yield of torrefied PKS was comparable with the torrefied reed canary grass. For example, the mass yield of torrefied PKS was 84.19% at 240 °C, while the mass yield of torrefied reed canary grass was 84% at 250 °C. Moreover, the mass yield of torrefied EFB was in the agreement of the torrefied sugarcane bagasse. The mass yield of torrefied EFB was 84.14% at 220 °C whereas the mass yield of torrefied sugarcane bagasse was 87.50% at 230 °C. However, the mass yield of torrefied EFB and PMF were lower compared than the others torrefied non-woody biomass especially torrefied reed canary grass and lucerne. The study had also reported that the mass yield of torrefied PKS, reed canary grass and lucerne were higher than others torrefied non-woody biomass.

Table 4.10 Comparison mass and energy yield with others non-woody biomass.

Non-woody biomass	Temperature (°C)	Time (h)	Mass yield (%)	Energy yield (%)	References
EFB	220	2.0	84.14	86.40	Present study
	240	2.0	71.99	78.08	
	260	2.0	62.22	70.75	
	280	2.0	47.50	59.23	
	300	2.0	42.84	55.70	
PMF	220	2.0	75.21	81.44	Present study
	240	2.0	71.65	79.27	
	260	2.0	64.38	73.56	
	280	2.0	54.63	66.32	
	300	2.0	45.50	59.46	
PKS	220	2.0	86.84	90.84	Present study
	240	2.0	84.19	89.15	
	260	2.0	76.08	83.81	
	280	2.0	74.65	86.50	
	300	2.0	61.05	73.79	
Reed canary grass	230	0.5	92.60	93.50	Bridgeman et. al. 2008
	250	0.5	84.00	86.60	
	270	0.5	72.00	77.10	
	290	0.5	61.50	69.00	
Bamboo	220	1.0	91.00	96.10	Rousset et. al. 2011
	250	1.0	76.00	88.40	
	280	1.0	57.00	78.00	
Sugarcane bagasse	230	1.0	87.50	96.42	Pach et. al. 2002
	250	1.0	78.90	92.03	
	280	1.0	68.60	82.90	
Lucerne	230	1.0	87.00	88.28	Chew and Doshi 2011
	250	1.0	81.60	83.06	
	280	1.0	71.60	77.31	

Furthermore, the energy yield of torrefied PKS was comparable with the energy yield of torrefied sugarcane bagasse. For instance, at the temperature of 220 °C, the energy yield of torrefied PKS was 90.84% while the mass yield of torrefied sugarcane bagasse was 92.03% at the temperature of 250 °C. The energy yield of torrefied EFB also was in the agreement of the energy yield of torrefied reed canary grass. The energy yield of torrefied EFB was 86.40% at 220 °C whereas the energy yield of torrefied reed canary grass was 86.60% at 250 °C. However, the study has found that the torrefied EFB and PMF have produced lower energy yield than others torrefied non-woody biomass especially the torrefied sugarcane bagasse and bamboo. Thus, the study had found that the energy yield of torrefied PKS, sugarcane bagasse and bamboo were higher than others torrefied non-woody biomass.

4.4.6 Microscopic Observation by SEM

The changes on the surface structure of biomass due to torrefaction process can be observed in the SEM images of EFB, PMF and PKS as illustrated in Figures 4.26 to 4.28. All the images were recorded at 5000x magnification for the selected particle size of 355-500 μm at torrefaction temperatures of 220, 260 and 300 °C. The particle size of 355-500 μm was only selected to perform this analysis due to the limited amount of particle size of 250-355 μm. From the SEM images of raw biomass, the study had found that the surface structure of raw EFB had exhibited sharp edges. However, the presence of sharp edges did not exist on the surface of both raw PMF and PKS. It can be suggested that the presence of sharp edges on the surface of raw EFB might be related with the grinding effect. The sharp edges maybe formed during the sample preparation process where the raw EFB was grinding by the grinder. Furthermore, the presence of pores can be observed on the surface of both raw EFB and PMF. Especially, pores of fibres were seen obviously on the surface of PMF. However, pores were not obviously seen on the surface of raw PKS. While for the raw PKS, the particles seem to be agglomerated. Besides, the surface of raw PKS was coarser than both raw PMF and PKS.

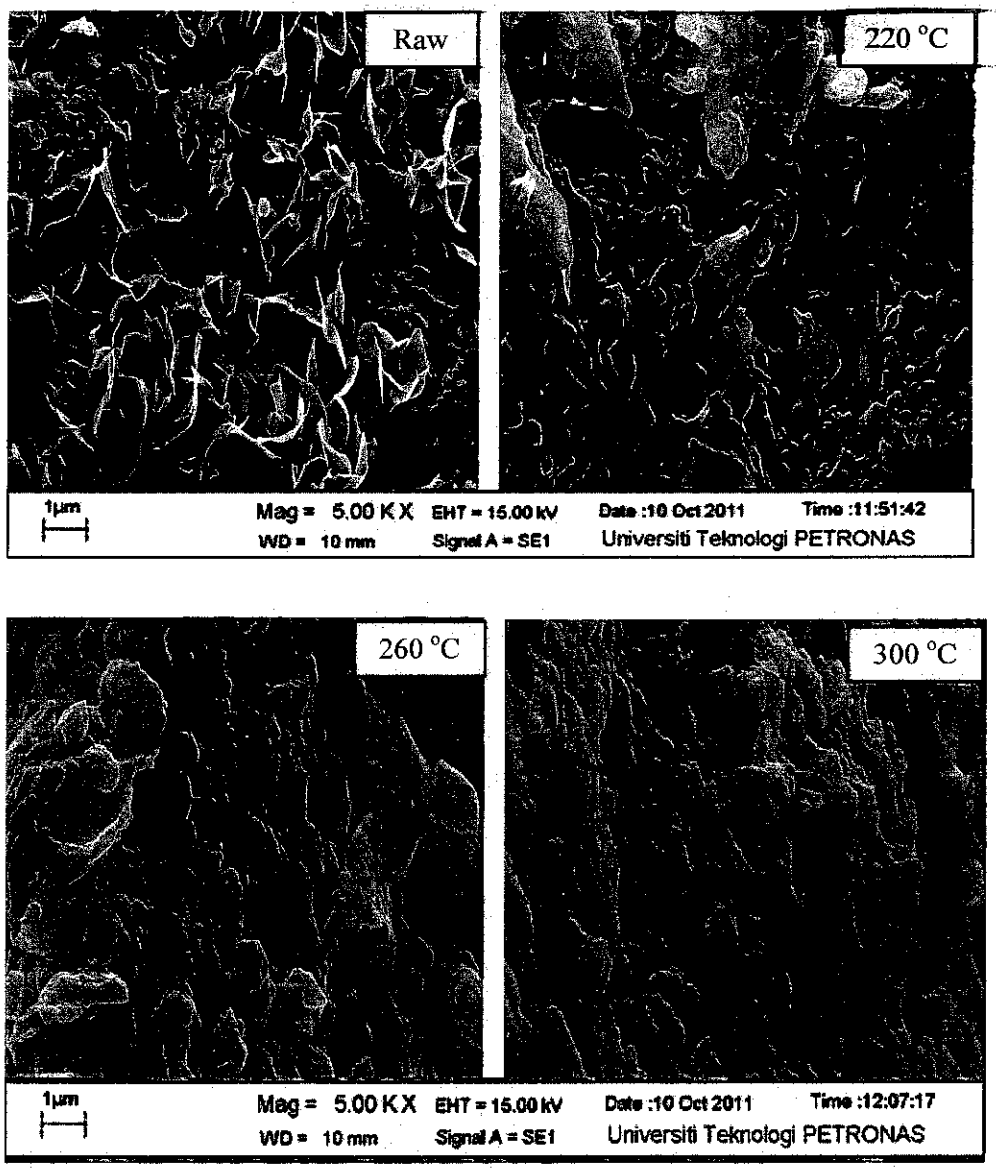


Figure 4.26 SEM images for raw and torrefied EFB size of 355-500 µm.

As mild torrefaction went further to severe torrefaction process, the changes on the surface structure for each torrefied biomass can be clearly observed when compared to the raw biomass. Increasing torrefaction temperature enhanced the impact of thermal pretreatment on the biomass and consumed more tiny particles. These observations were in the good agreement with the previous studies (Chen et. al., 2011a; Almeida et. al., 2010). During torrefaction process, the destruction of OH groups in the biomass by dehydration reactions causes the loss of capacity to form hydrogen bonds with water which makes the torrefied biomass hydrophobic. The torrefied biomass also becomes more porous and fragile since they loose its mechanical strength, making it easier to be grinded or milled.

The study had reported that the internal structure of both torrefied EFB and PMF were the most affected by torrefaction process as can be seen in Figures 4.26 to 4.27. The impact of the torrefaction temperatures on the internal structure both torrefied EFB and PMF can be clearly observed especially at the temperatures of 260 and 300 °C. The observations at 260 and 300 °C showed that the internal structure of both torrefied EFB and PMF were completely decomposed under severe torrefaction conditions. The presence of the sharp edges on the surface of raw EFB had almost flattened and disappeared while the presence of pores on the surface of raw PMF had been diminished.

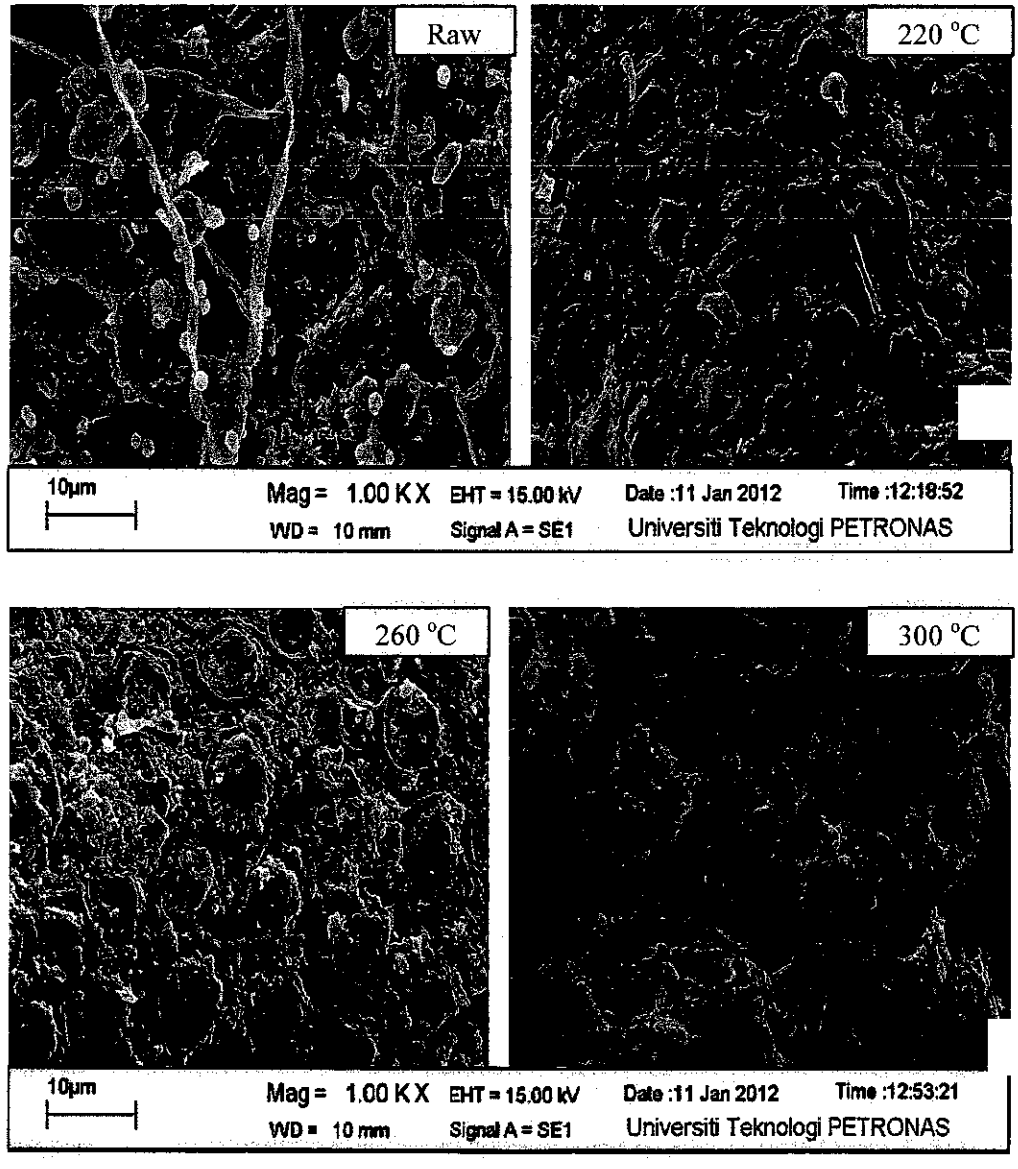


Figure 4.27 SEM images for raw and torrefied PMF size of 355-500 µm.

As reported from the lignocellulosic analysis in this study, both torrefied EFB and PMF contained higher amount of hemicellulose than PKS. Thus, they were presumed to start having decomposition at lower temperature of 150 °C while at higher temperature of 300 °C, the severe decomposition has occurred on the internal structure both of them. Therefore, the changes of internal structure of both torrefied EFB and PMF were affected by decomposition temperature of hemicellulose. Also, the study had reported that the internal structure of torrefied PKS was the least affected as can be observed in Figures 4.28. The observations at 260 and 300 °C have showed that the internal structure of torrefied PKS did not differ so much, only slight changes has occurred.

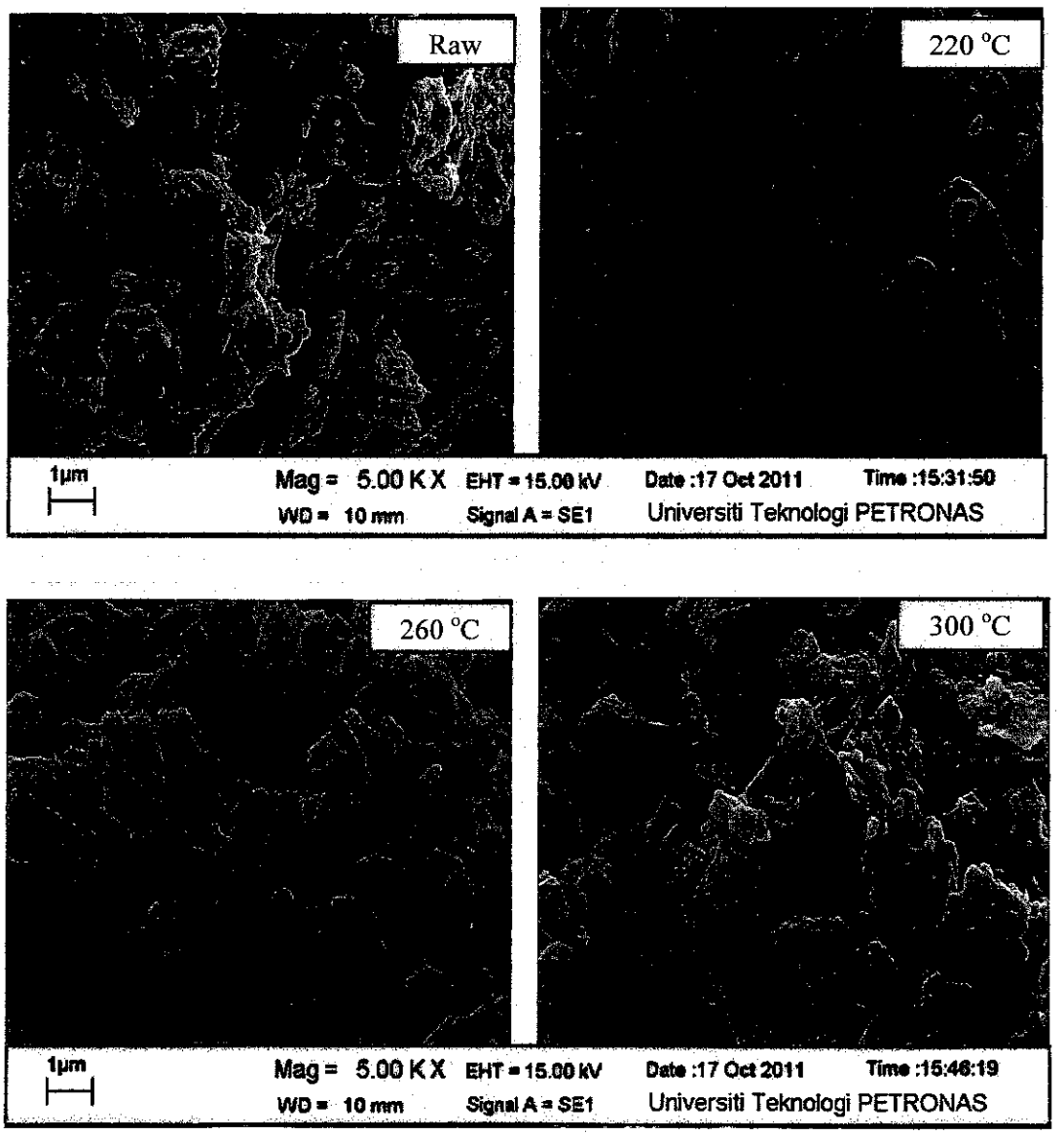


Figure 4.28 SEM images for raw and torrefied PKS size of 355-500 µm.

PKS has showed impact of decomposition to the internal structure due to its high lignin content as reported by the lignocellulosic analysis. Since the lignin has wider range of the decomposition temperature, which has started at the temperature of 250-500 °C. The decomposition of PKS has only started at 260 °C and 300 °C, the decomposition of lignin was still not completed. Therefore, the changes of internal structure of torrefied PKS was not clearly observed since it was significantly affected by decomposition temperature of lignin. The study had concluded that increasing the torrefaction temperature will enhance the impact on the decomposition of the internal structure of both torrefied EFB and PMF. However, torrefaction temperature had slightly impact on the decomposition of the internal structure of torrefied PKS.

In addition, decomposition temperature of hemicellulose and lignin also gave significant impact on these observations. These observations from the present study were in line with the previous studies by Chen et. al. (2011a). They reported that the torrefaction temperature and decomposition temperatures of hemicellulose and lignin gave significant influence to the decomposition behaviour of the internal structure of bamboo. The impact of torrefaction on internal structure of bamboo was clearly observed in Figure 2.21. They have also stated that the structure of torrefied bamboo at 290 °C was completely decomposed than to the structure of torrefied bamboo at 260 °C. In summary, all these observations from the present study were in line with the previous study.

4.5 Modeling for Torrefaction Process of Oil Palm Biomass

4.5.1 Kinetic Parameters

In the modeling work, the data of weight loss from torrefaction process in the TGA was used to calculate kinetic parameters. The kinetic of torrefaction reaction was assumed to follow the Arrhenius law such as the activation energy and rate constant. The determination of reaction order, n was obtained by using graphical approach method. The graphs are attached in Appendix A. The graphs with straight line have been obtained when plotting $\ln \frac{[W(t)]}{[W(0)]}$ versus time for all types of biomass.

Therefore, the study has assumed that both step reactions were first order reaction. Besides, the slope of these graphs were the rate constant, k_1 or k_2 and it have been used to determine the activation energy, E_a and pre-exponential factor, A. The activation energy, E_a and pre-exponential factor, A were obtained by plotting the graph of ln k_1 or ln k_2 versus $1/T$ which was the derivation from the Arrhenius equation as illustrated in Eq. 4.5.

$$k_1 \text{ or } k_2 = Ae^{\frac{-Ea}{RT}} \tag{4.5}$$

$$\ln k_1 \text{ or } \ln k_2 = \left(\frac{-Ea}{R}\right)\frac{1}{T} + \ln A$$

$$y = mx + c$$

where in J mol^{-1}, R was gas constant in J mol^{-1} K^{-1}, T was temperature in K and A was pre-exponential factor in s^{-1}. From the graphs, the value of activation energy over gas constant represented by the slope of the graphs, m and the value of pre-exponential factor represented by the intercept of the graphs, c. The graphs are attached in Appendix B.

In general, all the kinetic parameters have been obtained from the torrefaction process with a low heating rate of 10 °C min^{-1} and taking account the weight loss during the heating, drying and intermediate heating phases. If the heating rate was too high, the results might be affected by heat transfer limitations within the biomass. However, if too slow heating rate was applied, the weight loss that took place during the warm-up phase was not negligible, which can complicate the interpretation process of the kinetic data (Prins et. al., 2006b). Therefore, the heating rate of 10 °C min^{-1} was a common value used by researchers and suitable for TGA's system due to the relatively short warm-up phase.

Furthermore, the kinetic parameters were expressed in the form of Arrhenius equation which same as in Eq. 4.5 and listed in Table 4.11. From this table, it showed the calculated value of pre-exponential factor, A and activation energy, E_a in the expression of rate constant, k_1 or k_2 for EFB, PMF and PKS at each particle sizes. For instance, in order to calculate the value of rate constant, k_1 or k_2, value of

torrefaction temperature and value of gas constant need to be inserted. In the good agreement of studies by Prins et. al. (2006b), it has been reported that the first reaction stage was remarkably faster than the second stage. The study had also found that during torrefaction process, the first stage was always faster reaction than the second stage as expressed in Eqs. 4.6 and 4.7.

Table 4.11 Obtained value of pre-exponential factor, A and activation energy, E_a in the expression of rate constant, k_1 or k_2 for EFB, PMF and PKS.

Biomass types	Rate constant, k
EFB size 250-355 μm	$k_1 = 11 \times 10^3 \exp\left(\frac{-58267}{RT}\right)$ $k_2 = 1.24 \times 10^{-6} \exp\left(\frac{-34247}{RT}\right)$
EFB size 355-500 μm	$k_1 = 2.52 \exp\left(\frac{-20969}{RT}\right)$ $k_2 = 1.08 \times 10^{-6} \exp\left(\frac{-36134}{RT}\right)$
PMF size 250-355 μm	$k_1 = 25 \times 10^3 \exp\left(\frac{-63007}{RT}\right)$ $k_2 = 31.41 \exp\left(\frac{-39967}{RT}\right)$
PMF size 355-500 μm	$k_1 = 15 \times 10^3 \exp\left(\frac{-70938}{RT}\right)$ $k_2 = 68 \times 10^3 \exp\left(\frac{-70473}{RT}\right)$
PKS size 250-355 μm	$k_1 = 2.11 \times 10^6 \exp\left(\frac{-83817}{RT}\right)$ $k_2 = 8.94 \exp\left(\frac{-35062}{RT}\right)$
PKS size 355-500 μm	$k_1 = 66 \times 10^3 \exp\left(\frac{-69550}{RT}\right)$ $k_2 = 37 \exp\left(\frac{-42536}{RT}\right)$

Furthermore, the study has also suggested that there were two stages of decomposition reaction for the torrefaction process of oil palm biomass. The first stage was fast reaction while the second stage was slow reaction as illustrated in Eqs. 4.6 and 4.7. Moreover, the first stage represented the hemicellulose decomposition while the second stage represented further charring of the hemicellulose fraction.

First step (fast): $A(s) \xrightarrow{k_1} B(s)$ (4.6)

Second step (slow): $B(s) \xrightarrow{k_2} C(s)$ (4.7)

where A is initial feedstock, B is intermediate product and C is torrefied product; k_1 and k_2 are the rate constant for each stages.

4.5.2 Modelling work by MATLAB

In order to predict the amount of torrefied product that produced by EFB, PMF and PKS at the different torrefaction temperature and size, a model for torrefaction process of these biomass was developed through MATLAB. All the kinetic parameters were identified and coded into MATLAB software. The details coding are attached in Appendix C. However, before the coding work was done, the equation of rate of reaction was derived from Eqs. 4.5 and 4.6. The derivation was calculated from the initial weight of feedstock, $W_A(0)$ until the final weight product, W_C as follow:

$$\frac{dW_A}{dt} = -k_1 W_A(0)$$

$$\frac{dW_A}{W_A} = -k_1 dt$$

Then, integrate from time of 0 to time of t_1:

$$\int_0^{t1} \frac{dW_A}{W_A} = -\int_0^{t1} k_1 dt$$

$$\frac{\ln(W_A(t1))}{W_A(0)} = -k_1 t_{t1}$$

$$W_A(t1) = W_A(0) e^{(-k_1 t_{t1})}$$

Then, the value of $W_A(t_1)$ was directly substituted into Eq. 4.8:

$$\frac{dW_B}{dt} = k_2 W_A(t1) - k_2 W_B \tag{4.8}$$

Then, integrate from the time of 0 to time of t_2,

$$\int_0^{t2} dW_B = \int_0^{t2} [(k_1 W_A(0) e^{(-k_1 t_{t2})}) - (k_2 W_B)] dt$$

By applying the Laplace transform which attached in Appendix D,

$$W_B(t2) = \frac{k_1}{k_2 - k_1} \times W_A(0) \times (e^{(-k_1 t_{t2})} - e^{(-k_2 t_{t2})})$$

The value of W_B (t_2) was substituted into Eq. 4.8:

$$\frac{dW_C}{dt} = k_2 W_B(t2) \tag{4.9}$$

The, integrate from time of 0 to time of t_3,

$$\int_0^{t2} dW_C = \int_0^{t3} [k_2 W_B(t2)] dt$$

$$\int_0^{t2} dW_C = \int_0^{t2} \left[k_2 \left(\frac{k_1}{k_2 - k_1} \times W_A(0) \times (e^{(-k_1 t_{t2})} - e^{(-k_2 t_{t2})}) \right) \right] dt$$

By applying Laplace transform in Appendix D,

$$W_C(t3) = \frac{k_2 k_1}{k_2 - k_1 + k_2} \times W_A(0) \times (e^{(-k_1 t_{t2})} - e^{(-k_2 t_{t2})} - e^{(k_2 t_{t3})})$$

The W_A (t_1), W_B (t_2) and W_C (t_3) were coded into MATLAB. After that, MATLAB was run and the amounts of torrefied biomass (EFB, PMF and PKS) were predicted by MATLAB. The amount of torrefied biomass (in wt. %) for EFB, PMF and PKS that have been predicted by MATLAB are presented in Tables 4.12 to 4.17; respectively. In addition, the comparison between the experimental data with model data are also plotted in the same graphs for EFB, PMF and PKS as illustrated in Figures 4.29 to 4.34. Besides, the AAD was also calculated in order to study the deviations of the results between the experimental and modelling data.

4.5.3 Comparison between the Experimental and Model Data

The graphs of biomass weight that have been predicted by model and experimental data of EFB, PMF and PKS for each particle size are illustrated in Figures 4.29 to 4.34. The figures were plotted with the starting time of 17 minutes because torrefaction process has started after minutes of 17. It was because at the time less than 17 minutes, the temperature was less than 200 °C, and was not accounted as torrefaction process. It can be observed from the minutes of 17 to 77, the weight reduction was drastically decreased for all types of biomass. However, the weight reduction was slowly decreased after the minutes of 77. Meanwhile, after the minutes of 117, the curves were remained constant which indicating no more weight loss occurred and the decomposition of the biomass can be considered as completed. These observations have revealed that the distributions weight loss was influenced by the torrefaction temperature.

In addition, the study had also proposed there were two steps of reaction for the decomposition of oil palm biomass during torrefaction process. Torrefaction process from the minutes of 17 until 77 represented the first step which was the fast reaction as illustrated in Eq. 4.5. Besides, torrefaction process after the minutes of 77 represented the second step which was slow reaction as illustrated in Eq. 4.6. Moreover, the fast initial step represented the hemicellulose decomposition while the slow second step represented further charring of hemicellulose fraction. The study had also showed that the two decomposition steps of torrefaction oil palm biomass were comparable with the two decomposition steps of torrefaction wood as reported by Prins et. al. (2006b). Furthermore, the absolute average deviation (AAD) was introduced to calculate the deviation between the experimental and modeling data as shown in Eq. 4.10. In general, the calculated AAD was less than 5% for EFB, PMF and PKS for each particle size as listed in Tables 4.12 to 4.17. Therefore, the study has found that the developed model for EFB, PMF and PKS within particle size range of 255-500 μm were applicable caused the deviation was less than 5%.

$$\text{AAD (\%)} = \frac{\text{Experimental data} - \text{Modelling data}}{\text{Experimental data}} \times 100 \qquad (4.10)$$

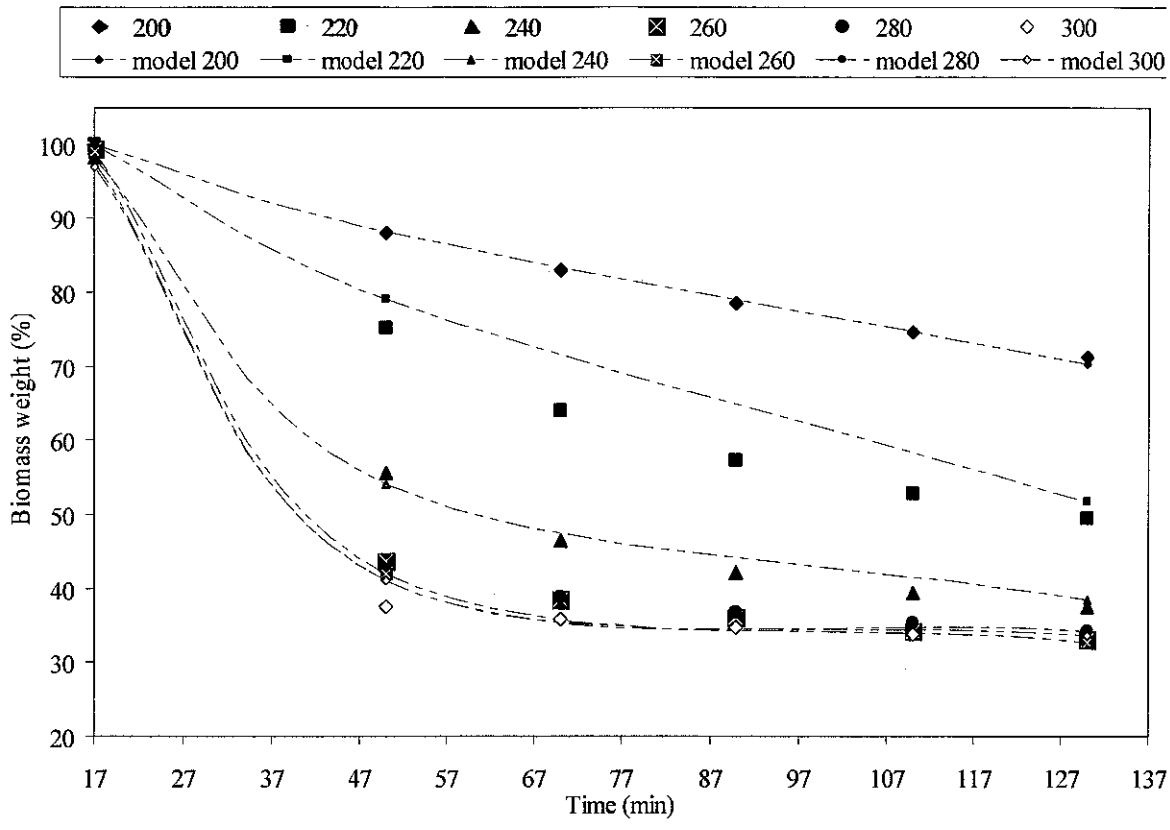


Figure 4.29 Experimental and model curves for EFB size of 250-355 μm.

Table 4.12 AAD between the experimental and modeling data for EFB 250-355 μm.

Temperature (°C)	Biomass weight (%) Experimental	Modelling	AAD (%)
200	71.17	70.24	1.30
220	49.51	51.71	4.43
240	37.46	38.54	2.86
260	32.98	32.68	0.89
280	34.24	34.15	0.27
300	32.93	33.66	2.22
AAD between experimental and modelling			2.00

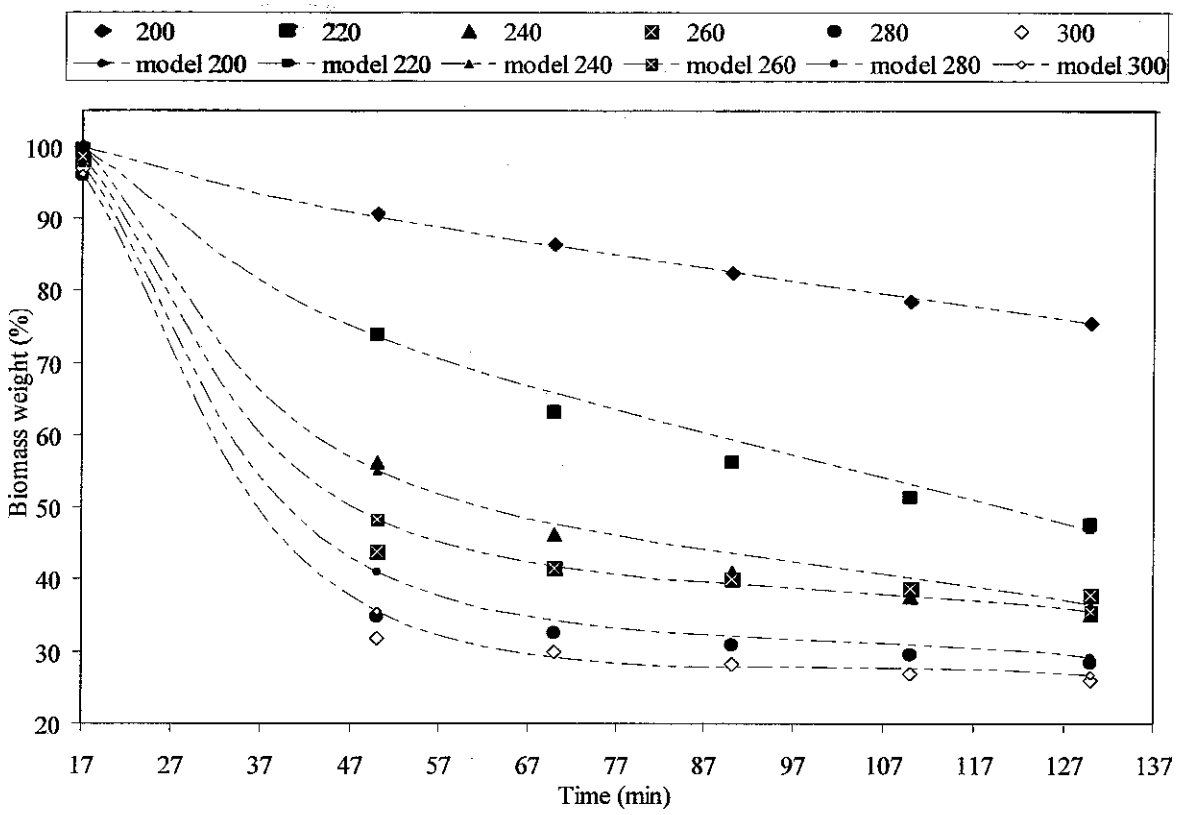


Figure 4.30 Experimental and model curves for EFB size of 355-500 μm.

Table 4.13 AAD between the experimental and modeling data for EFB 355-500 μm.

Temperature (°C)	Biomass weight (%) Experimental	Modelling	AAD (%)
200	75.61	75.61	0.00
220	47.66	46.83	1.74
240	35.12	36.59	4.17
260	37.80	35.61	5.81
280	28.54	29.27	2.56
300	26.00	26.83	3.19
AAD between experimental and modelling			2.91

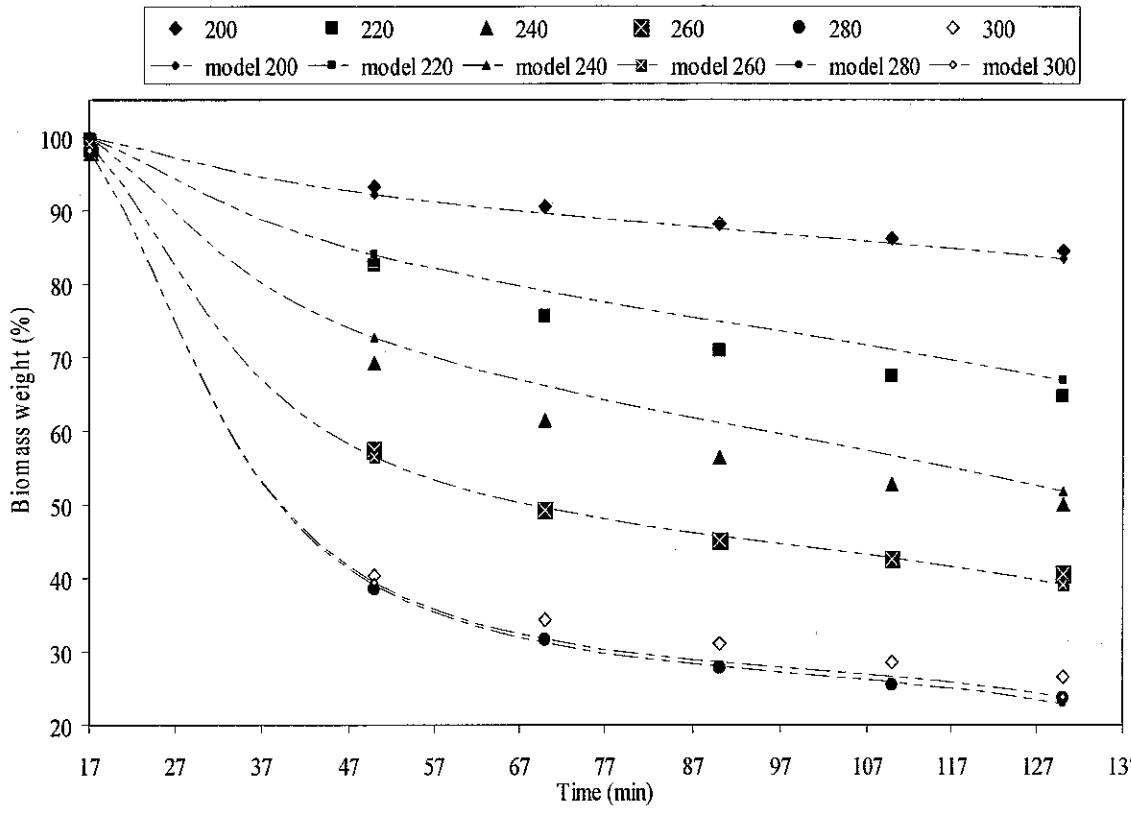


Figure 4.31 Experimental and model curves for PMF size of 250-355 μm.

Table 4.14 AAD between the experimental and modeling data for PMF 250-355μm.

Temperature (°C)	Biomass weight (%) Experimental	Modelling	AAD (%)
200	84.44	83.41	1.21
220	64.63	66.83	3.40
240	49.95	51.71	3.52
260	40.44	39.02	3.50
280	23.56	22.93	2.69
300	26.59	23.90	10.09
AAD between experimental and modelling			4.07

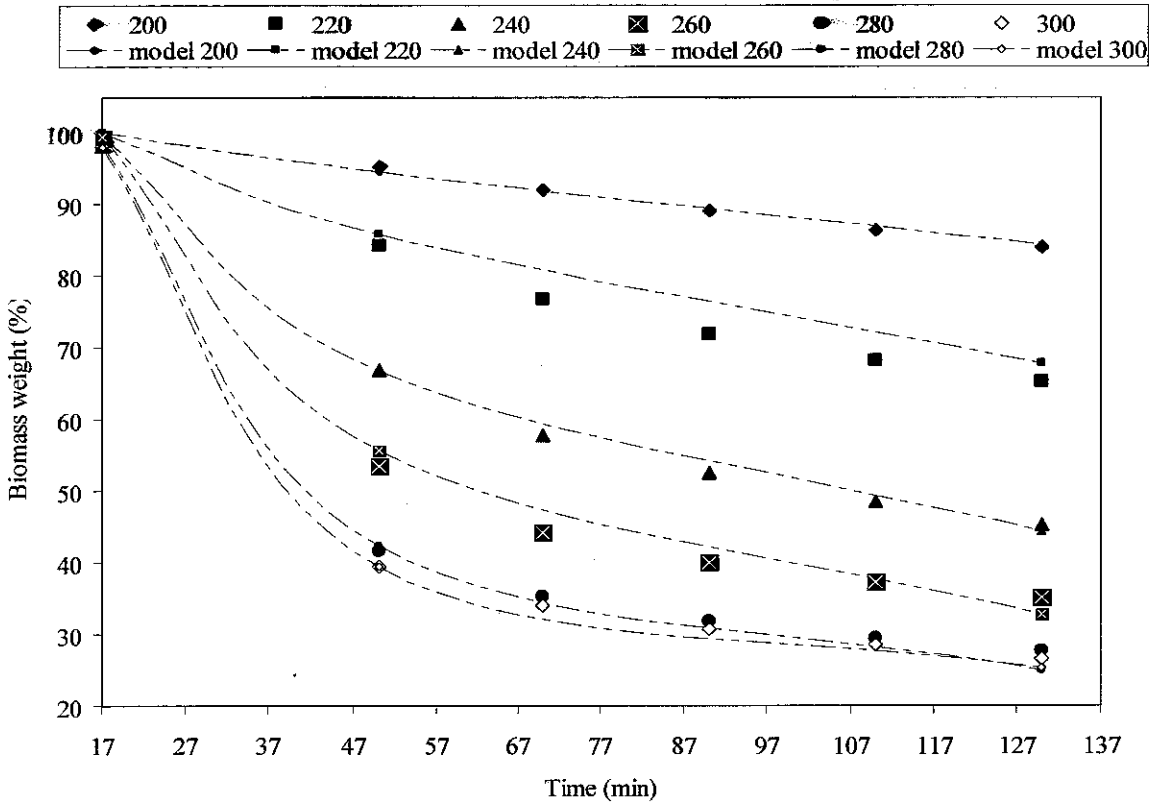


Figure 4.32 Experimental and model curves for PMF size of 355-500 μm.

Table 4.15 AAD between the experimental and modeling data for PMF 355-500 μm.

Temperature (°C)	Biomass weight (%)		AAD (%)
	Experimental	Modelling	
200	84.05	84.39	0.41
220	65.37	67.80	3.73
240	45.37	44.39	2.15
260	35.12	32.68	6.94
280	27.66	24.88	10.05
300	26.63	25.37	4.76
AAD between experimental and modelling			4.67

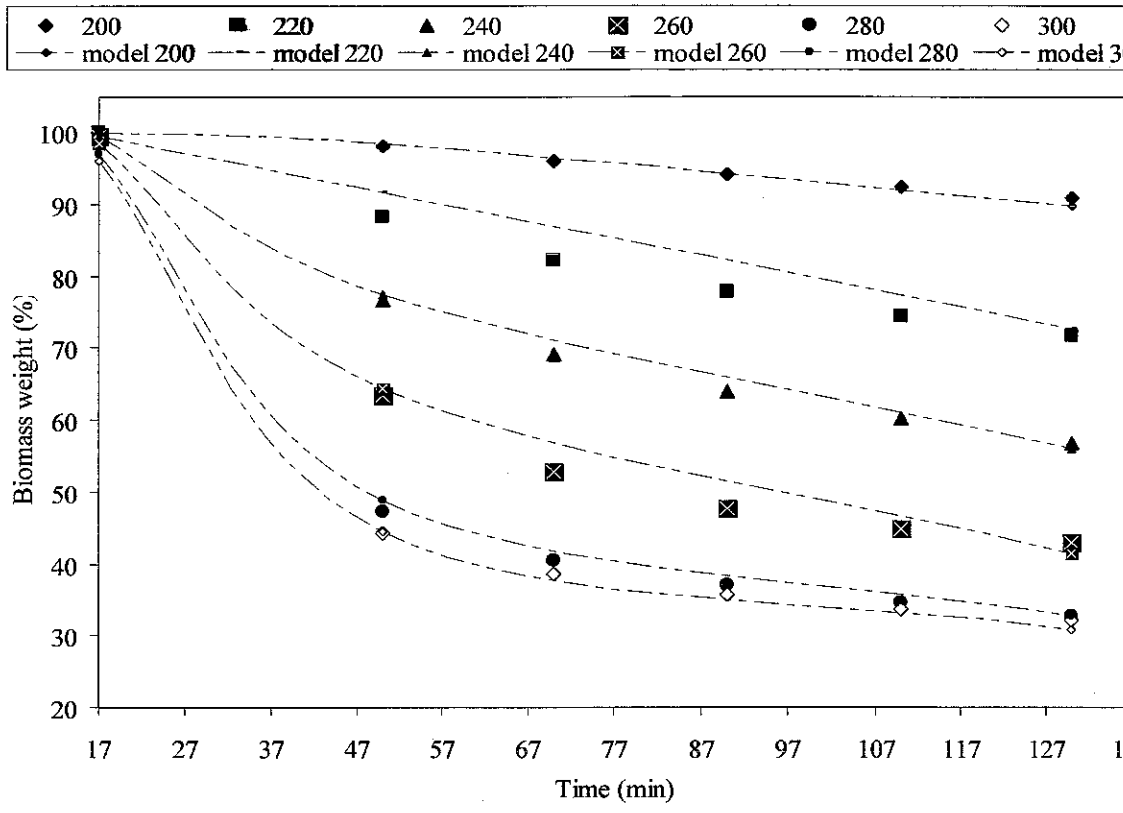


Figure 4.33 Experimental and model curves for PKS size of 250-355 μm.

Table 4.16 AAD between the experimental and modeling data for PKS 250-355 μm.

Temperature (°C)	Biomass weight (%) Experimental	Modelling	AAD (%)
200	91.02	89.76	1.39
220	71.71	72.68	1.36
240	56.78	56.10	1.20
260	42.93	41.46	3.41
280	32.78	32.68	0.30
300	32.10	30.73	4.26
AAD between experimental and modelling			1.99

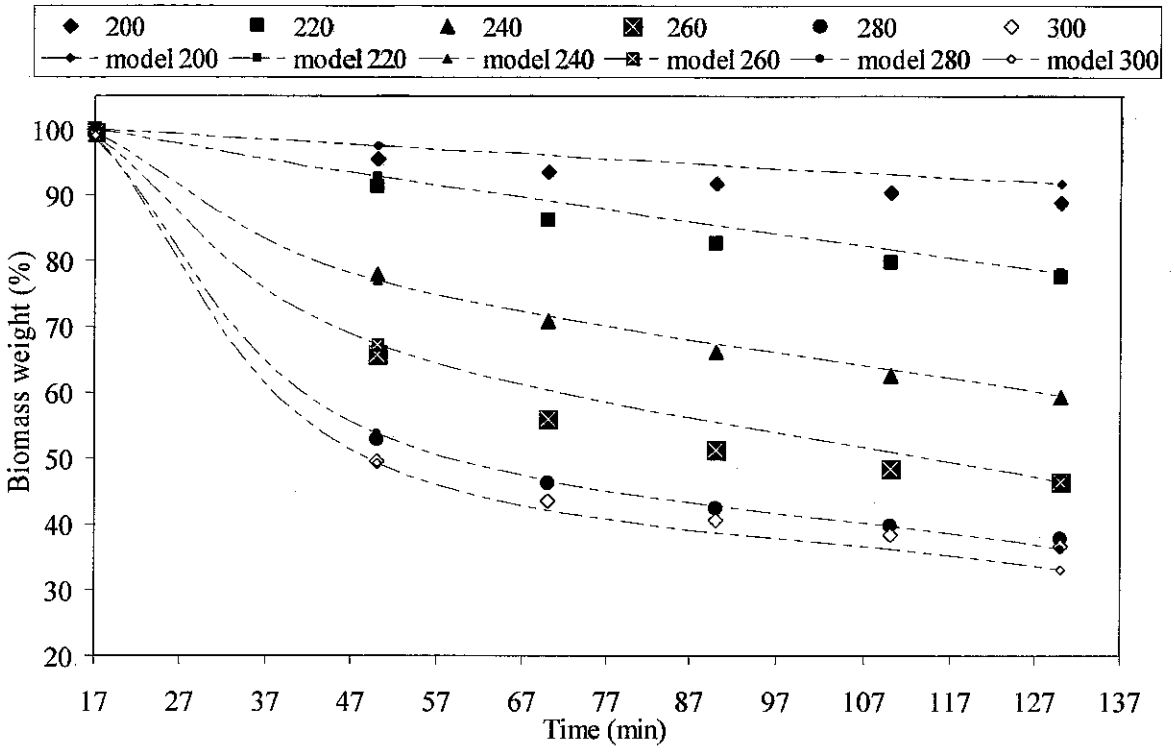


Figure 4.34 Experimental and model curves for PKS size of 355-500 μm.

Table 4.17 AAD between the experimental and modeling data for PKS 355-500 μm.

Temperature (°C)	Biomass weight (%)		AAD (%)
	Experimental	Modelling	
200	88.78	91.71	3.30
220	77.46	78.05	0.76
240	59.37	59.51	0.25
260	46.44	46.34	0.21
280	37.71	36.10	4.27
300	36.54	33.17	9.21
AAD between experimental and modelling			3.00

As the oil palm biomass is the lignocellulose biomass, the decomposition was affected by the hemicellulose, cellulose and lignin. The study had reported that both EFB and PMF were more significantly decomposed than PKS as mentioned in section 4.4.2. It was verified that the high content of hemicellulose in both EFB and PMF compared to PKS by lignocellulosic analysis. Due to high content of hemicellulose, it has enhanced the decomposition rate of the process. Chen and Kuo (2010a) have also reported that decomposition temperature of hemicellulose was within the range of 150 to 350 °C, which clearly showed that this decompositon temperature was in the ranges of torrefaction temperature. Therefore, severe decomposition has been occurred of both EFB and PMF during torrefaction process.

Biomass torrefaction process generally proceeds through a series of complex reaction pathways. At low heating rate, biomass materials decompose in well described stages of moisture evolution hemicellulose decomposition and cellulose decomposition as reported by Yang et. al. (2004). However, in the present study, it was found that the hemicellulose decomposition was the most significant and prominent than the cellulose decomposition. Yang et. al. (2004) had also reported that there was no interaction occurred among these three components. But, some researchers have believed that the mechanism of biomass torrefaction process was a superstition of the mechanism of these three components. One or all of these three components have been used as kinetic model biomass in the previous studies. In this study, only hemicellulose decomposition was considered in the kinetic model.

In the literatures, two types of kinetic model have been applied for the decomposition of whole lignocellulose biomass (Vahergyi et. al., 1989). The first approach was a formal description in which separate competitive reactions were assumed to describe product distribution, but the chemical in homogeneity of the biomass was not taken into account. In the second approach, the decomposition lignocellulose biomass was assumed to be the sum of decomposition of its components. They have concerning the independence of the decomposition of three components in the lignocellulose biomass. In the present study, the first approach which was an independent of hemicellulose decomposition was proposed and had been applied to develop a model.

4.6 The Added Value and Benefits of Torrefaction

Torrefaction aims for the production of fuel that has improved and upgraded properties as compared to the untreated biomass. In this study, it was found that the carbon content and GCV of torrefied biomass gradually increased as the torrefaction temperature increased. The study revealed that the torrefied PKS had the highest carbon content with 58.7% which was 22% higher than the untreated PKS. Meanwhile, PMF had the highest GCV with 23.73 MJ/kg which was 24% higher than the untreated PMF. This significant increment of the carbon content and GCV of PMF and PKS after pre-treat by torrefaction was very beneficial when during utilization such as gasification or pyrolysis. Higher carbon content and GCV will produce higher energy density of the final products during energy conversion process such as pyrolysis or gasification.

Furthermore, the energy yield of torrefied PKS can be maintained at 86-92% under mild to severe torrefaction process, up to 280 °C. Thus, this work suggested that for the industry, PKS should not be torrefied at higher temperature, more than 280 °C in order to preserve its energy yield around 90%. However, the energy yield of both torrefied EFB and PMF only can be maintained at 70-78% under mild torrefaction process, up to 240 °C. This significant finding would recommend that in the industry, both EFB and PMF should not be torrefied at higher temperature, more than 240 °C in order to preserve their energy yield around 70-80%. This basic knowledge on the effect of torrefaction temperature on the energy yield produced was very important in the large scale production of torrefied oil palm biomass. It is because torrefaction process aims to maintain the energy content of the torrefied biomass without losing too much chemical energy to the volatile products during the process. Therefore, energy yield was very crucial parameter in order to achieve an efficient and economic energy conversion process.

In addition, the study suggested that the industry should not conduct torrefaction process at 300 °C for all type of oil palm biomass. It is because, it would produced torrefied biomass with very low energy yield which was less than 70% and caused very high mass loss which was more than 45%. Too much loss in the mass and

energy yields is not favourable since it can significantly reduce the efficiency during energy conversion process. Moreover, the moisture uptake of torrefied biomass is very limited due to the dehydration during the torrefaction reaction. Destruction of OH groups in the biomass by dehydration causes the loss of capacity to form hydrogen bonds with water. Thus, a non-polar unsaturated structures are formed which makes the torrefied biomass hydrophobic.

After torrefaction process, the fibrous structure and tenancy of biomass are reduced due to the hemicellulose decomposition together with the depolymeristation of cellulose and lignin. It can significantly decrease the electricity consumption for milling. The power consumption in the size reduction is decreased 70-85% when the biomass is first torrefied (Uslu et. al., 2008). Moreover, the capacity of the mill increases in proportion to the particle size. When the 0.2 mm particle size is considered, the chipper capacity for torrefied willow is up to 6.5 times the capacity of untreated biomass. Besides, a simpler type of size reduction, such as cutting mills can be employed instead of hammer mill which used in the conventional process.

Additionally, due to torrefied biomass becomes more porous and fragile as it looses its mechanical strength, it is easier to grind or pulverise and increase the homogeneity of torrefied biomass (Arias et. al., 2008). It also improved the grindability and friability hence, enhanced the ignitibility and reactivity during energy conversion process. Moreover, the homogenous particles of the torrefied biomass can be used in the pulverised systems, such as co-firing with coal in the boilers and gasification in the entrained flow gasifier (Bridgeman et. al., 2008; Deng et. al., 2009). The torrefied biomass had become suitable feedstock for the entrained flow gasification, which previously the raw biomass was not considered feasible. It was because the torrefied biomass form became more spherical shaped particles during the grinding process (Bergman et. al., 2005b).

Other than that, the pre-treatment technology has a significant influence on the performance of bioenergy chains, especially on the logistics. For instance, torrefaction, pyrolysis and pelletisation technologies can convert biomass at modest scales into dense energy carriers that ease the transportation and handling. Uslu et. al. (2008) have reported that torrefaction is a very promising technology due to its high process efficiency (94%) compared to pelletisation (84%) and pyrolysis (64%). Finally, the study had concluded that torrefaction process of oil palm biomass is a very promising technology in order to achieve an efficient and economic energy conversion process such as pyrolysis and gasification.

4.7 Chapter Summary

In the present work, torrefaction behaviour of three kinds of oil palm biomass which were empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) have been studied. TGA was used to study the weight loss of biomass during torrefaction process while tube furnace was used to produce significant amount of torrefied biomass for further analysis. The characterizations of raw materials such as calorific value, lignocellulosic, ultimate and proximate analyses have been presented. Besides, the impacts of torrefaction temperature to the composition and decomposition temperature of hemicellulose, cellulose and lignin upon the properties of torrefied biomass are discussed. The discussion on the CHNS content, calorific value, weight loss distributions, mass and energy yield, mass loss and surface structure are also highlighted. The mass loss had been proposed as a good indicator for the severity of torrefaction process. Moreover, the kinetic studies of torrefaction process which includes the developed model and the comparison between the modelling data with experimental data are presented. Finally, the advantages or added values of torrefied oil palm biomass from these findings and its benefits for an industrial scale are also discussed.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Chapter Overview

The chapter presents the major conclusions of the present work. It also includes the proposed recommendations that can be applied for further research work.

5.2 Conclusion

In Malaysia, oil palm biomass are the most abundant agricultural wastes that are sulphur, nitrogen negligible, CO_2 neutral and highly potential as renewable energy. Torrefaction process of empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) at particle sizes of 250-500 μm have been performed under two different conditions which were mild torrefaction (200, 220 and 240 °C) and severe torrefaction (260, 280 and 300 °C). The study suggested that torrefaction process were divided into two main stages. The first stage was dehydration process at the temperature below 105 °C with weight reduction was in the range of 3-5%. While in the second stage, the decomposition reaction took place at temperature of 200-300 ° C. Specifically, the weight reduction was in the range of 45-55% which can be observed for all types of biomass. The study had revealed that the carbon content and GCV of torrefied biomass were increased as the torrefaction temperature increased. The PKS had the highest carbon content with 58.7% while PMF had the highest GCV with 23.73 MJ/kg. However, as the torrefaction temperature increased, the O/C ratio, hydrogen and oxygen content were decreased. The exception was the nitrogen content which it remained less than 2% for all torrefaction conditions. As for sulphur content, at any torrefaction conditions, it always approaches to zero.

In this study, both EFB and PMF have the highest mass loss compared to PKS after severe torrefaction process. The mass loss for both EFB and PMF were 56% while only 39% for PKS at 300 °C. Furthermore, the study had obtained good correlations between the mass loss with the carbon content and GCV. Thus, the study had proposed that mass loss was an excellent indicator for the torrefaction process severity. Due to the high mass loss of both EFB and PMF, they also have lower mass yield compared to PKS. The energy yield of PKS can be maintained in the range of 86-92% from mild to severe torrefaction process, up to 280 °C. However, the energy yield of both EFB and PMF were in the range of 70-78% only at mild torrefaction process, up to 240 °C. Moreover, the SEM images have verified that the impact of torrefaction on the internal structure of both EFB and PMF were more significant than PKS under severe torrefaction process. In general, these differences properties and characteristics of the torrefied oil palm biomass were dependant upon four factors which were torrefaction temperature, biomass types, and composition and decomposition temperatures of the hemicellulose, cellulose and lignin. Depending on which of the properties of the torrefied oil palm biomass that needs to be optimized, these four factors should be considered.

In addition, torrefaction process at the temperature of 300 °C was not recommended since it caused very high mass loss which was more than 45% and produced very low energy yield which was less than 70%. Besides, based on the kinetic studies, a two-stage decomposition reaction was proposed to describe the torrefaction process of EFB, PMF and PKS within size range of 255 to 500 μm. The first step was fast reaction (from the minutes of 17 until 77) which represented the hemicellulose decomposition while the second step was slow reaction (after the minutes of 77) which represented further charring of the hemicellulose fraction. Other than that, the biomass weight of the experimental data and developed model data were plotted in the same graph in order to compare these results. The calculated AAD had revealed that the deviation between the experimental data and developed model data was below than 5%. Therefore, this developed model was successfully applicable only for the torrefaction process of EFB, PMF and PKS within particle sizes range of 255 to 500 μm.

5.3 Recommendations

During torrefaction process, there are few recommendations can be applied in order to further investigate torrefaction process of oil palm biomass as follows:

(a) Focus on the polymeric composition of the feed biomass and after torrefaction. Chemical analysis of the hemicellulose, cellulose and lignin content of the torrefied biomass can be considered. Knowledge about the relationship between the polymeric composition and torrefaction characteristics such as mass and energy yield and production volatiles would be very important for the development of predictive tools to optimize the process. Besides, TGA analysis can be carried out to predict which constituents is the most decomposable by the torrefaction process.

(b) Further optimization of the torrefaction conditions is recommended to increase the quality for optimal feeding. Torrefaction temperature and biomass particle size are considered the most important parameters in this aspect. It is also important to investigate the particle size effects since it can significantly influence by the heat transfer during the torrefaction process.

(c) Perform the quantitative and qualitative analysis on the torrefaction gases such as CO_2, CO, CH_4 and H_2 by using Gas Chromatography-Mass Spectrometry (GC-MS). The significant on doing this analysis is to determine major and minor gases released by the torrefaction process. For instance, it is known that combustion of oil palm biomass will produce more CO_2 and CO. It is very important to determine the amount these greenhouse gases, thus can reduce their emission to environment especially in the large scale or industry.

5.4 Chapter Summary

The thesis ends with this chapter where the conclusions of all major findings have been highlighted and briefly presented. Some recommendations have been proposed for further undertaking in this research area.

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PUBLICATIONS

Journals

- Muafah A. Aziz, Khalik M. Sabil, Yoshimitsu Uemura and Lukman Ismail
  A Study on Torrefaction of Oil Palm Biomass.
  Journal of Applied Sciences, vol. 12 (11), pp. 1130-1135, 2012.
- Muafah A. Aziz, Khalik M. Sabil and Yoshimitsu Uemura
  Characterization of Empty Fruit Bunches (EFB) and Kernel Shell after Torrefaction.
  Journal of Applied Sciences, submitted.
- Muafah A. Aziz, Khalik M. Sabil, Yoshimitsu Uemura
  Effects of torrefaction on the Properties of Empty Fruit Bunches (EFB), Palm Mesocarp Fiber (PMF) and Palm Kernel Shell (PKS)
  Biomass and Bioenergy, submitted.
- Muafah A. Aziz, Khalik M. Sabil, Yoshimitsu Uemura
  Potential of Mass Loss as an Excellent Indicator of Intensity of Torrefaction Oil Palm Biomass.
  Applied Energy, submitted.

Conference Proceedings/ Book of Abstracts

- Muafah A. Aziz, Khalik M. Sabil and Yoshimitsu Uemura
  Characterization of Oil Palm Biomass as Feed for Torrefaction in Proceeding of the 2nd National Postgraduate Conference (NPC 2011), 19-20 Sept 2011, Universiti Teknologi PETRONAS (UTP), Perak, Malaysia.
- Muafah A. Aziz, Khalik M. Sabil and Yoshimitsu Uemura
  A Study on Torrefaction of Oil Palm Biomass in the Proceeding of 25th Symposium of Malaysian Chemical Engineers (SOMChe 2011), 29 Nov-1 Dec 2011, Kuantan, Pahang, Malaysia.

- Muafah A. Aziz, Khalik M. Sabil and Yoshimitsu Uemura
  Kinetics Torrefaction of Empty Fruit Bunch (EFB), Mesocarp Fiber and Kernel Shell of Oil Palm in the Proceeding of 24th International Symposium on Chemical Engineering (ISCE 2011), 2-4 Dec 2011, Gyeong-ju, Korea.
- Muafah A. Aziz, Khalik M. Sabil and Yoshimitsu Uemura
  Characterization of Empty Fruit Bunches (EFB) and Kernel Shell after Torrefaction in the Proceeding of 2nd International Conference on Process Engineering and Advanced Materials (ICPEAM 2012), 12-14 June 2012, Kuala Lumpur, Malaysia.

APPENDIX A

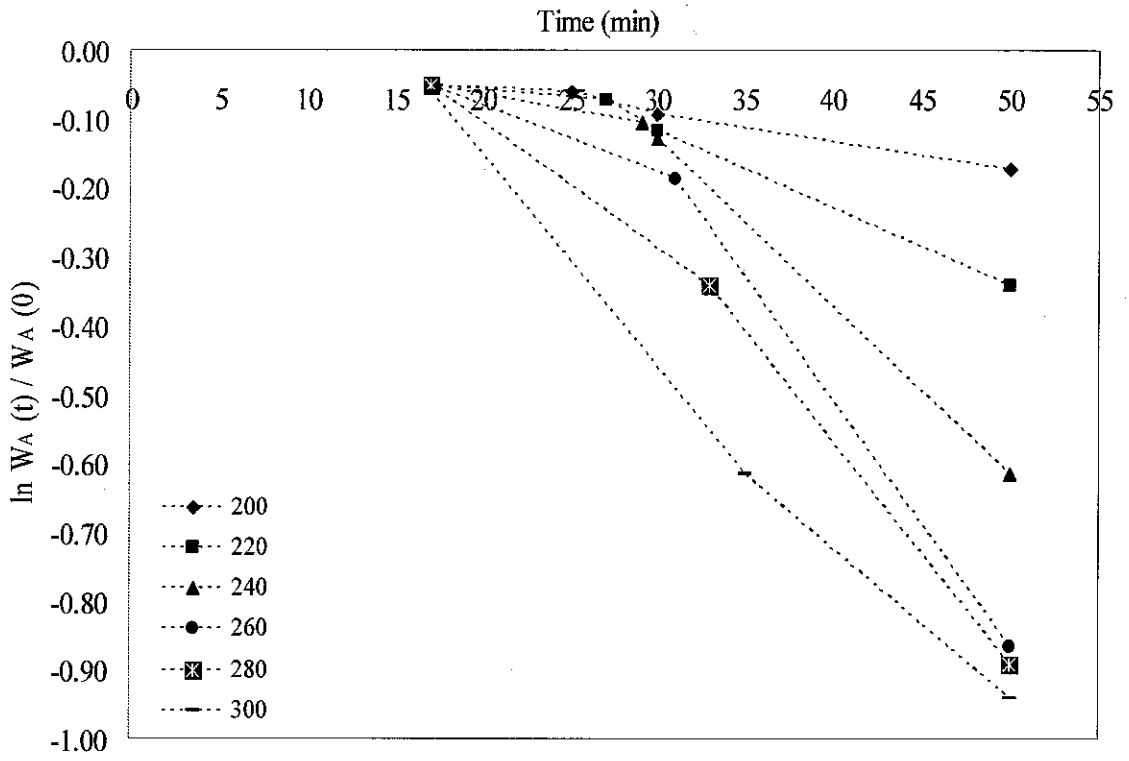

Figure A.1 Graphs of determination of reaction order, n=1 by graphical approach for EFB size of 250-355 μm.

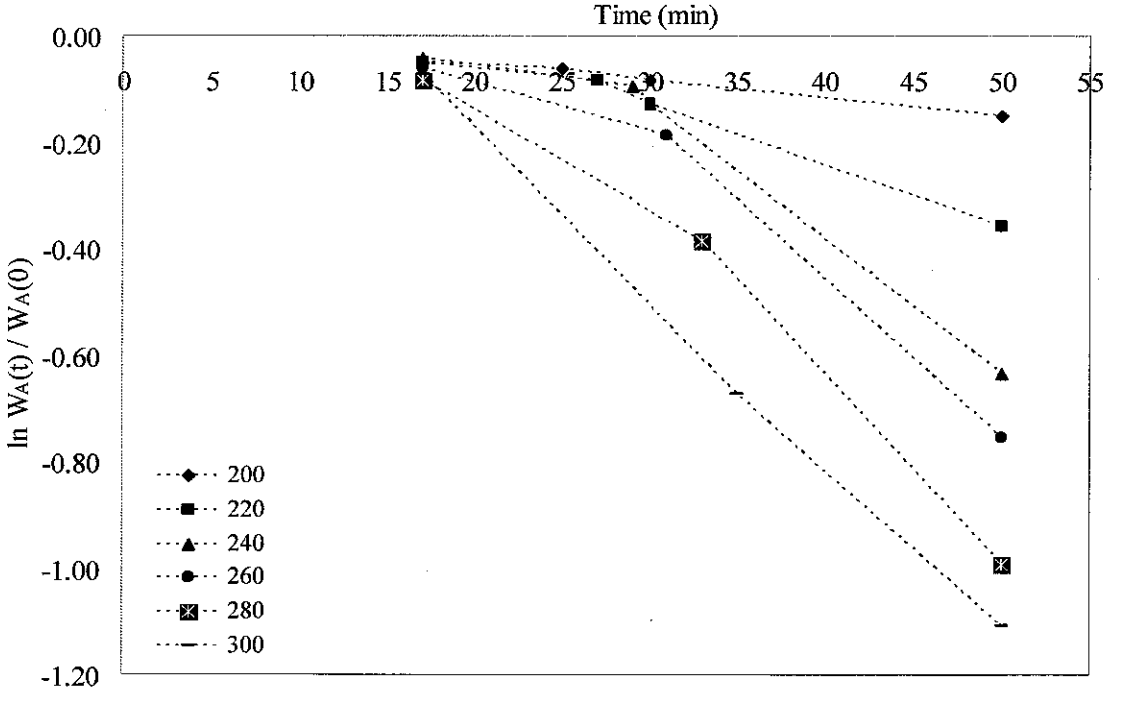

Figure A.2 Graphs of determination of reaction order, n=1 by graphical approach for EFB size of 355-500 μm.

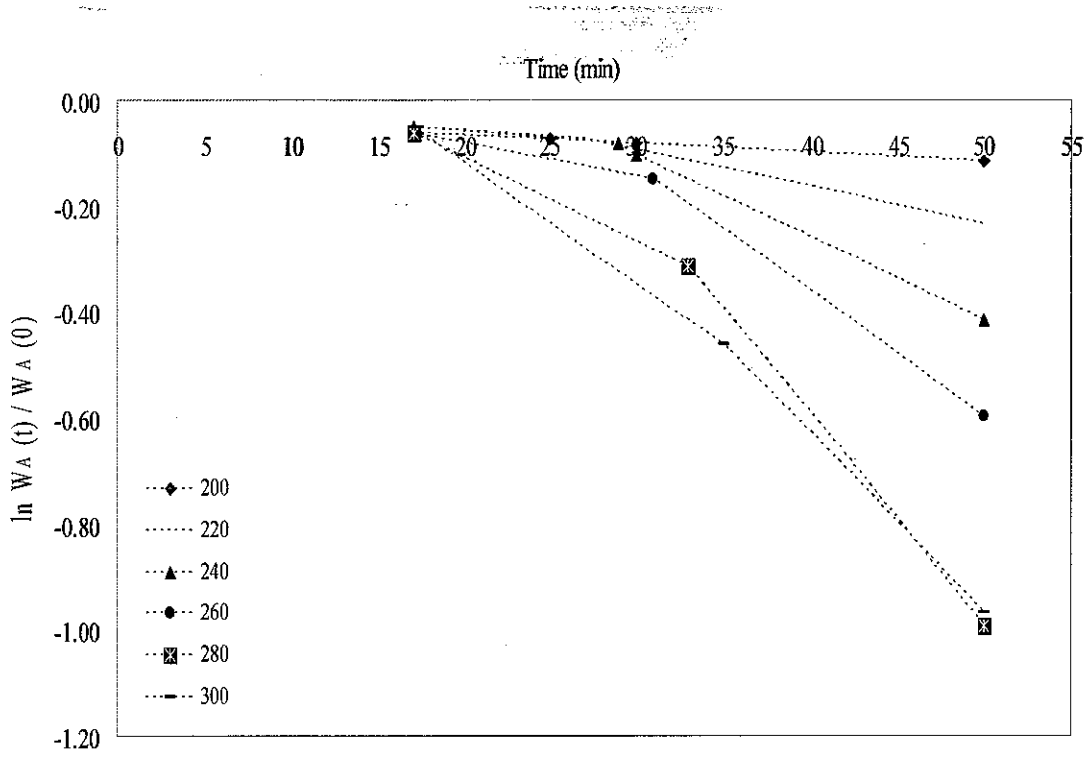

Figure A.3 Graphs of determination of reaction order, n=1 by graphical approach for PMF size of 250-355 μm.

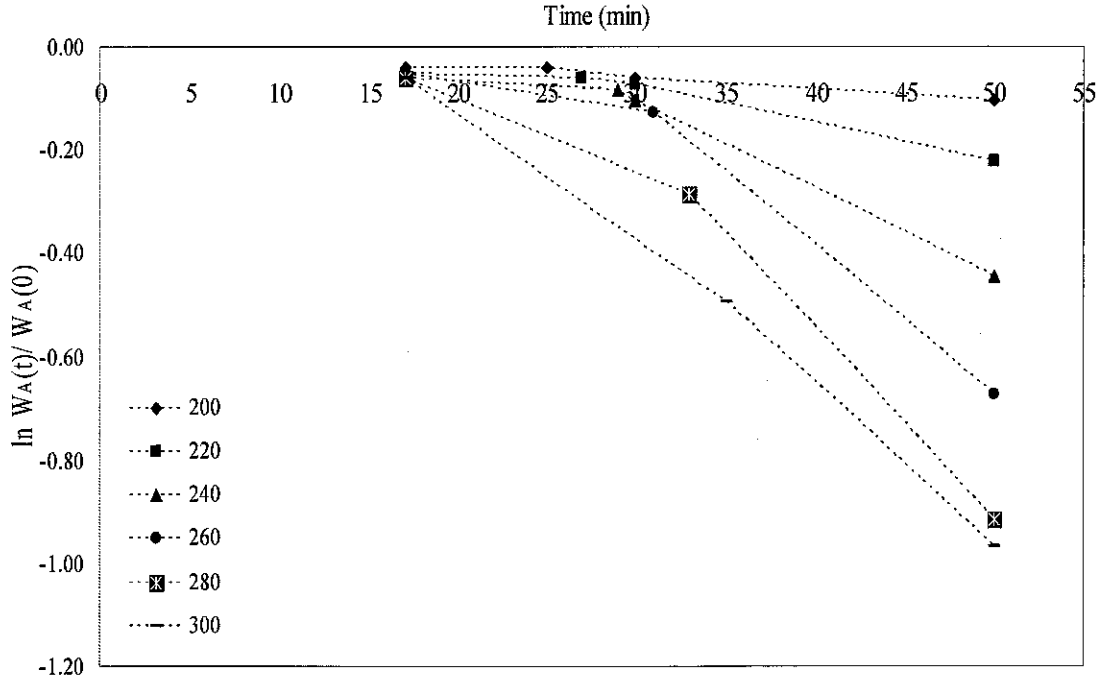

Figure A.4 Graphs of determination of reaction order, n=1 by graphical approach for PMF size of 355-500 μm.

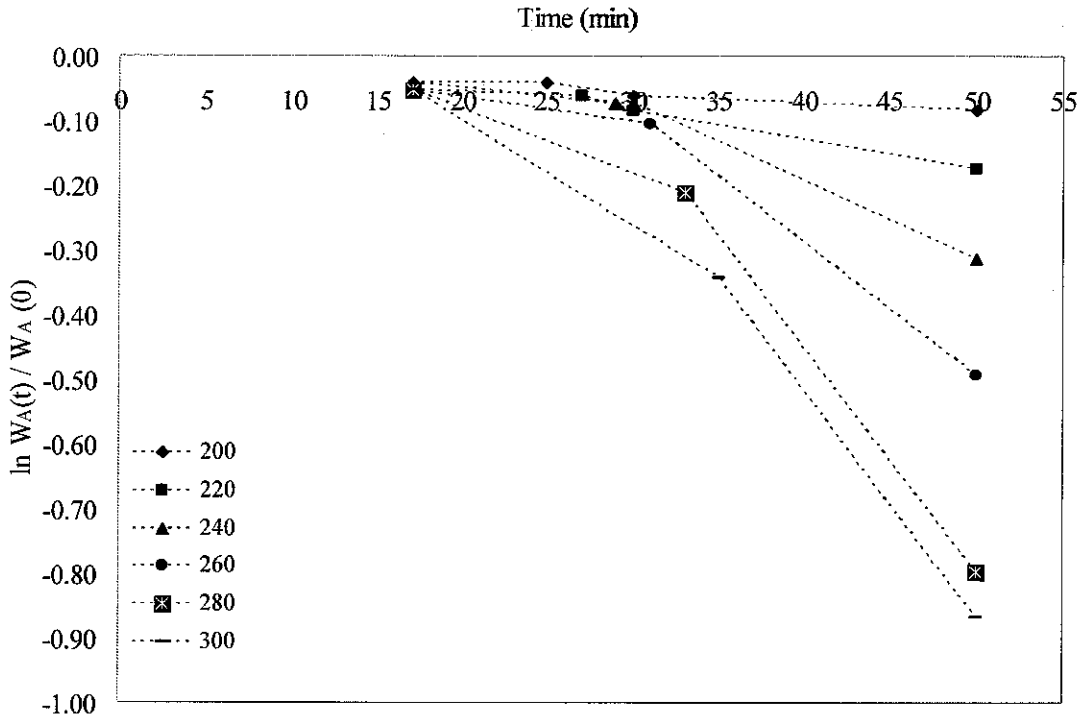

Figure A.5 Graphs of determination of reaction order, n=1 by graphical approach for PKS size of 250-355 μm.

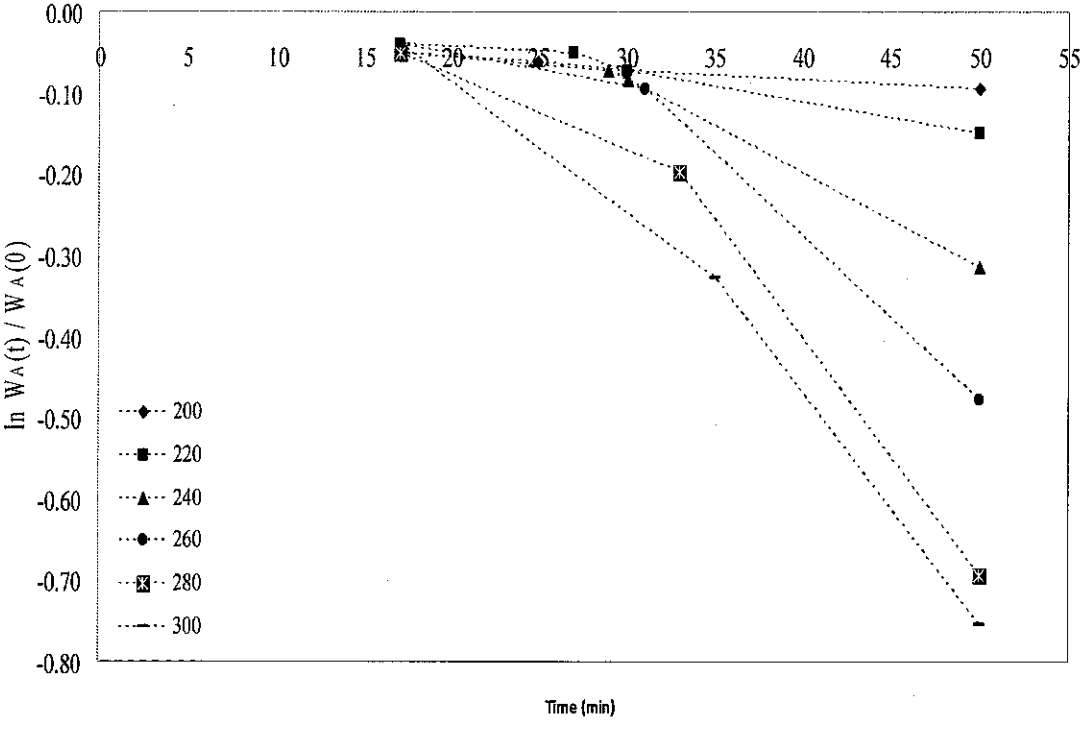

Figure A.6 Graphs of determination of reaction order, n=1 by graphical approach for PKS size of 355-500 μm.

APPENDIX B

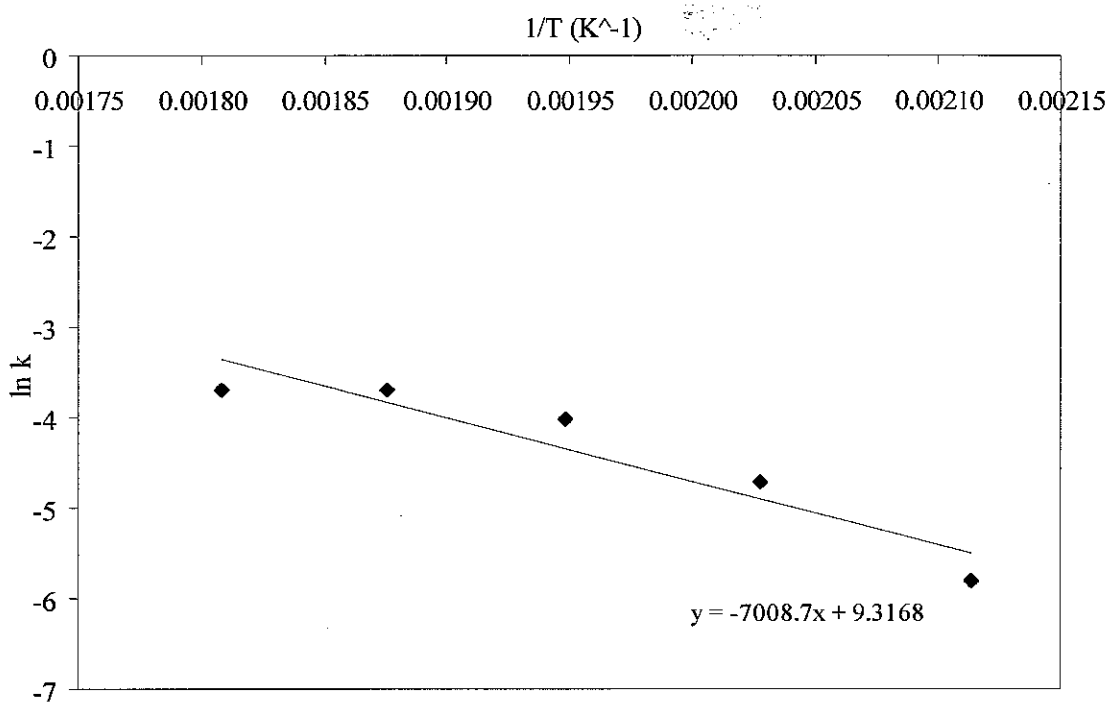

Figure B.1 Graph of determination of the pre-exponential factor, A and activation energy, E_a by using k_1 for EFB size of 250-355 μm.

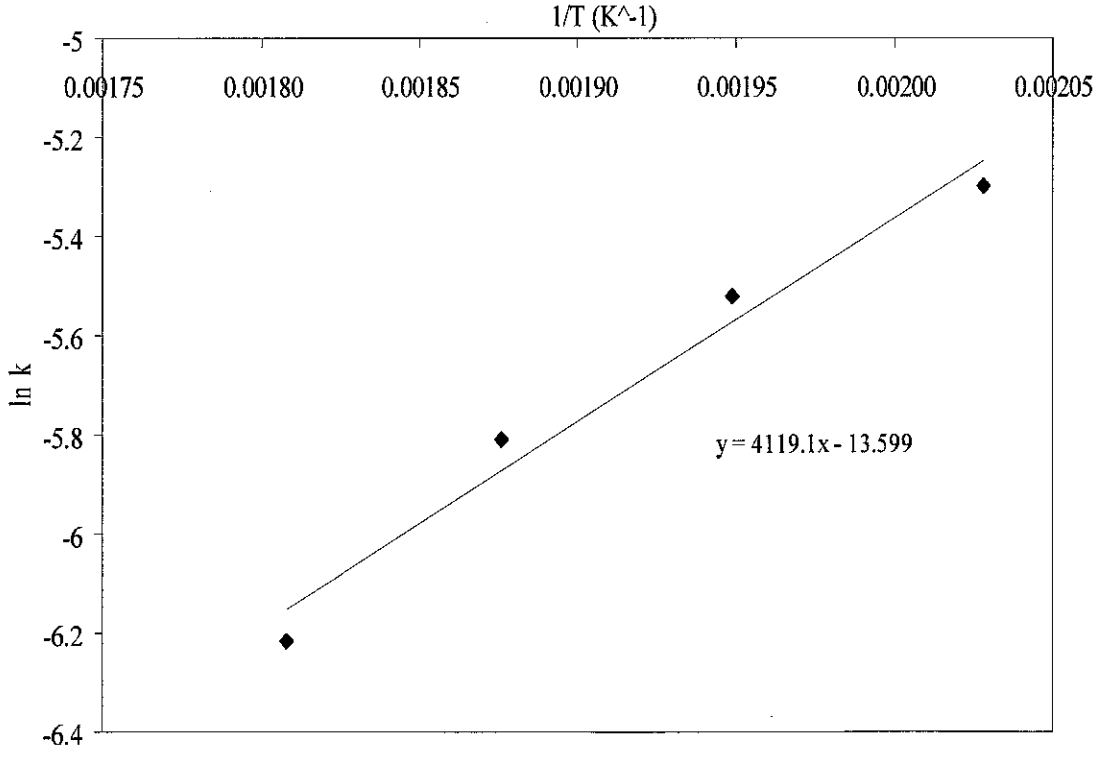

Figure B.2 Graph of determination of the pre-exponential factor, A and activation energy, E_a by using k_2 for EFB size of 355-500 μm.

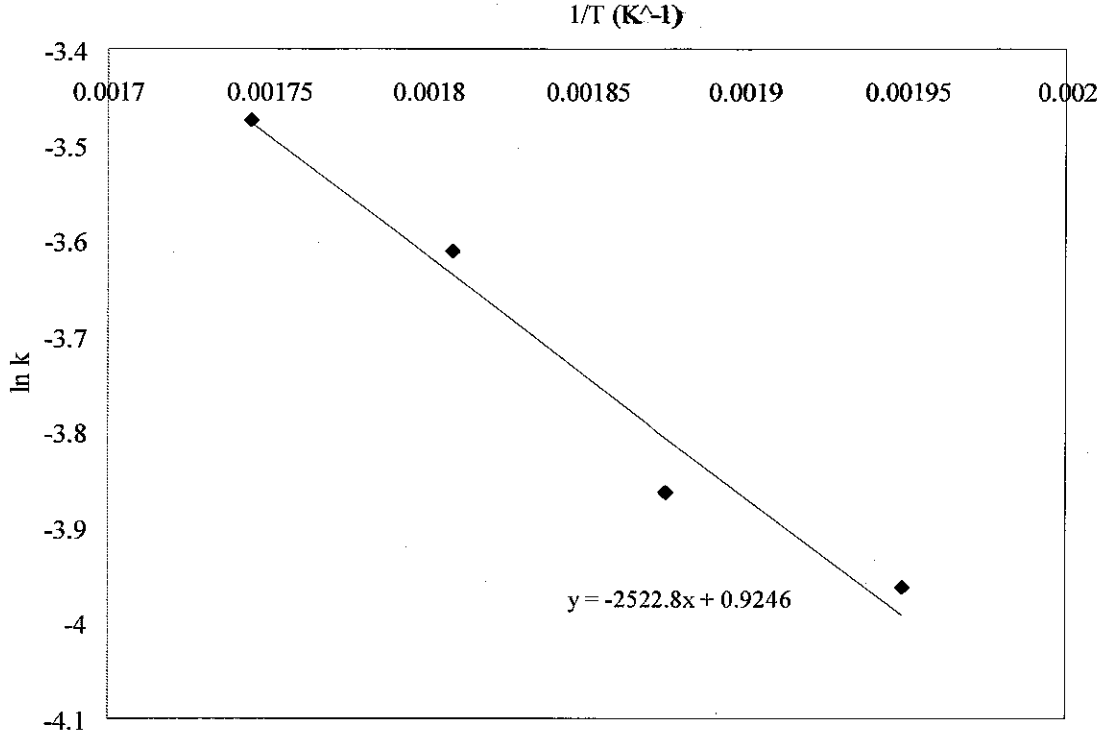

Figure B.3 Graph of determination of the pre-exponential factor, A and activation energy, E_a by using k_1 for PMF size of 250-355 μm.

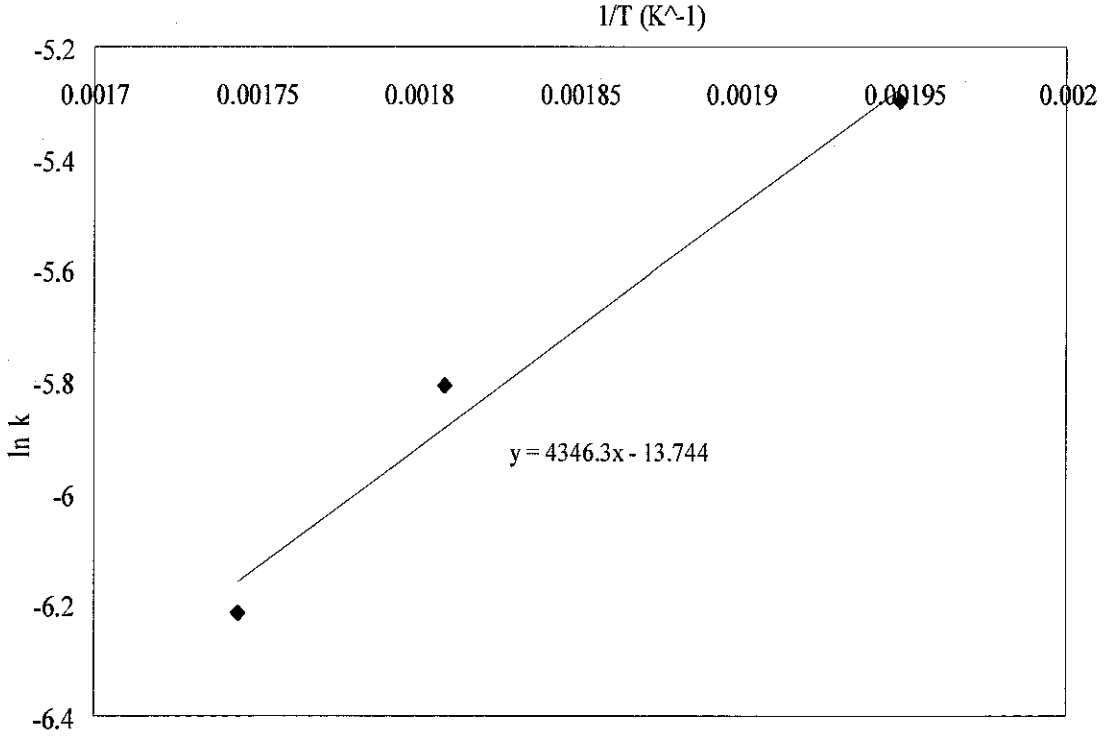

Figure B.4 Graph of determination of the pre-exponential factor, A and activation energy, E_a by using k_2 for PMF size of 355-500 μm.

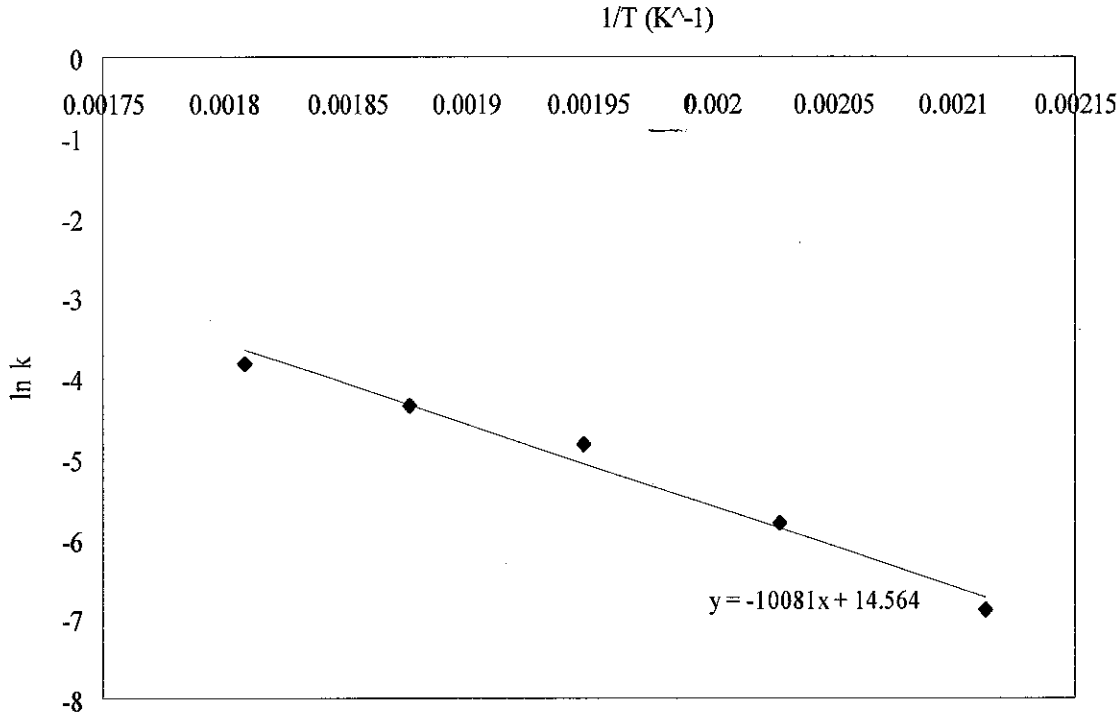

Figure B.5 Graph of determination of the pre-exponential factor, A and activation energy, E_a for PKS size of 250-355 μm.

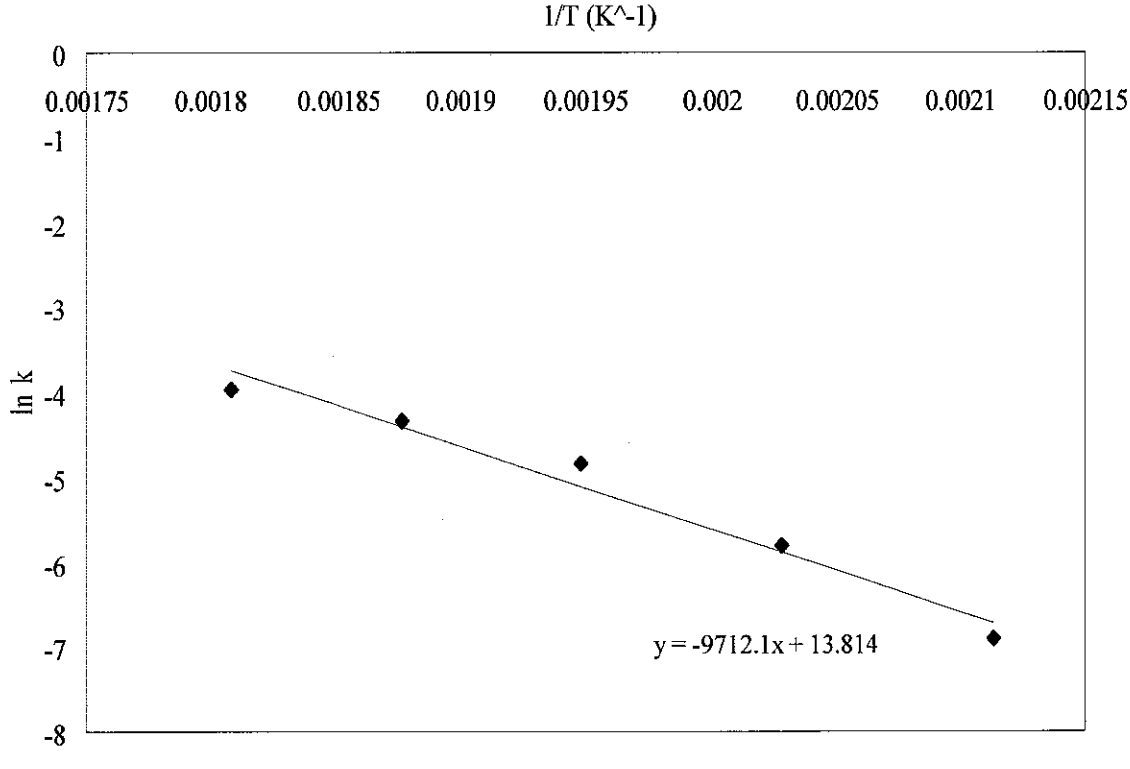

Figure B.6 Graph of determination of the pre-exponential factor, A and activation energy, E_a for PKS size of 355-500 μm.

APPENDIX C

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\EFB_355.m

```
function Biomass=EFB_355(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=33;tc=30;
elseif T==220
    tb=33;tc=80;
elseif T==240
    tb=46;tc=90;
elseif T==260
    tb=40;tc=90;
elseif T==280
    tb=25;tc=90;
elseif T==300
    tb=16;tc=120;
end
%Formulation
T1=T+273.15;
kw1=0.44*exp(-18383/(R*T1));
kw2=0.001;
k1=11E03*exp(-58267/(R*T1));
k2=1.24E-06*exp(34247/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\EFB_355.m

```
%Output print out at main screen
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.1 Coding for torrefaction of EFB size of 250-355 μm.

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\EFB_500.m

```
function Biomass=EFB_500(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=10;tc=17;
elseif T==220
    tb=21;tc=63;
elseif T==240
    tb=32;tc=80;
elseif T==260
    tb=32;tc=80;
elseif T==280
    tb=33;tc=117;
elseif T==300
    tb=32;tc=135;
end
%Formulation
T1=T+273.15;
kw1=2.96*exp(-26889/(R*T1));
kw2=0.001;
k1=2.52*exp(-20969/(R*T1));
k2=1.08E-06*exp(36134/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
%Output print out at main screen
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\EFB_500.m

```
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.2 Coding for torrefaction of EFB size of 355-500 μm.

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PMF_355.m

```
function Biomass=PMF_355(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=33;tc=80;
elseif T==220
    tb=33;tc=1250;
elseif T==240
    tb=33;tc=125;
elseif T==260
    tb=33;tc=100;
elseif T==280
    tb=33;tc=100;
elseif T==300
    tb=20;tc=70;
end
%Formulation
T1=T+273.15;
kw1=0.198*exp(-15240/(R*T1));
kw2=0.001;
k1=25E03*exp(-63007/(R*T1));
k2=31.41*exp(-39967/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
%Output print out at main screen
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PMF_355.m

```
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.3 Coding for torrefaction of PMF size of 250-355 μm.

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PMF_500.m

```
function Biomass=PMF_500(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=33;tc=100;
elseif T==220
    tb=33;tc=100;
elseif T==240
    tb=42;tc=90;
elseif T==260
    tb=33;tc=67;
elseif T==280
    tb=27;tc=35;
elseif T==300
    tb=17;tc=17;
end
%Formulation
T1=T+273.15;
kw1=0.174*exp(-14725/(R*T1));
kw2=0.001;
k1=156E03*exp(-70938/(R*T1));
k2=68E03*exp(-70473/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
%Output print out at main screen
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PMF_500.m

```
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.4 Coding for torrefaction of PMF size of 355-500 μm.

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PKS 355.m

```
function Biomass=PKS_355(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=33;tc=80;
elseif T==220
    tb=33;tc=135;
elseif T==240
    tb=40;tc=135;
elseif T==260
    tb=33;tc=135;
elseif T==280
    tb=27;tc=90;
elseif T==300
    tb=16;tc=65;
end
%Formulation
T1=T+273.15;
kw1=0.98*exp(-21642/(R*T1));%ok
kw2=0.001;
k1=2.11E06*exp(-83817/(R*T1));
k2=8.94*exp(-35062/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
%Output print out at main screen
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PKS 355.m

```
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.5 Coding for torrefaction of PKS size of 250-355 μm.

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PKS 500.m

```
function Biomass_PKS_500(T,W)
%Constant
R=8.3144;n=1;
%Fixed time for torrefaction process
if T==200
    tb=33;tc=30;
elseif T==220
    tb=35;tc=150;
elseif T==240
    tb=50;tc=150;
elseif T==260
    tb=40;tc=150;
elseif T==280
    tb=34;tc=110;
elseif T==300
    tb=23;tc=80;
end
%Formulation
T1=T+273.15;
kw1=1.23*exp(-23472/(R*T1));
kw2=0.001;
k1=66E03*exp(-69550/(R*T1));
k2=37*exp(-42536/(R*T1));
WA=W*exp(-kw1*7);
WA1=WA*exp(-kw2*10);
WB=WA1*exp(-k1*tb);
WC=WB*exp(-k2*tc);
rA=k1*WA1^n;
rC=k2*WB^n;
%Output print out at main screen
```

C:\Program Files\MATLAB\R2008a\work\Torrefaction Model\PKS 500.m

```
if T==200
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==220
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==240
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==260
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==280
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
elseif T==300
    fprintf('Weight of Feed Enter          :%.4f kg \n',W);
    fprintf('Weight after moisture removal :%.4f kg \n',WA1);
    fprintf('Weight of Product             :%.4f kg \n',WC);
    fprintf('Rate of Formation Product     :%.4f kg/min \n',rC);
end
```

Figure C.6 Coding for torrefaction of PKS size of 355-500 μm.

APPENDIX D

Table D.1: Laplace Transform

TIME DOMAIN		FREQUENCY DOMAIN
$\delta(t)$	unit impulse	1
A	step	$\frac{A}{s}$
t	ramp	$\frac{1}{s^2}$
t^2		$\frac{2}{s^3}$
$t^n, n > 0$		$\frac{n!}{s^{n+1}}$
e^{-at}	exponential decay	$\frac{1}{s+a}$
$\sin(\omega t)$		$\frac{\omega}{s^2+\omega^2}$
$\cos(\omega t)$		$\frac{s}{s^2+\omega^2}$
te^{-at}		$\frac{1}{(s+a)^2}$
t^2e^{-at}		$\frac{2!}{(s+a)^3}$